

BULLETIN  
DE  
L'ACADÉMIE POLONAISE  
DES SCIENCES

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VOLUME III  
NUMÉRO 5

VARSOVIE 1955

PRINTED IN POLAND

PAŃSTWOWE WYDAWNICTWO NAUKOWE – DZIAŁ CZASOPISM  
WARSZAWA, KRAKOWSKIE PRZEDMIEŚCIE 79

Nakład 1052 + 103 egz.	Rękopiś dostarczono 22. IV. 1955
Ark. wyd. 3,0, ark. druk. 2,75	Podpisano do druku 20. VI. 1955
Papier bezdrzewny sat. 80 g. kł. III	Druk ukończono w czerwcu 1955
Format B5, 70×100 cm	Zam. prod. 171/55 Cena zł 5.–

KRAKOWSKA Drukarnia Naukowa, KRAKÓW, UL. CZAPSKICH 4

# Sur la force latérale exercée sur un obstacle par un liquide visqueux et compressible

par

A. KRZYWICKI

Présenté par H. STEINHAUS le 18 Mars 1955

Je considère le mouvement spatial \*) d'un liquide visqueux, compressible, remplissant tout l'espace à l'extérieur d'une surface fermée  $\Sigma$  de dimensions finies, qui sans se déformer, se déplace parallèlement à une droite avec une vitesse constante égale à  $W_0$ . Soit  $XYZ$  un système de coordonnées lié à la surface  $\Sigma$ , l'axe  $Z$  étant parallèle à la vitesse de  $\Sigma$ . Soient  $u, v, w$  — les composantes de la vitesse du liquide par rapport au système immobile, parallèle au système  $XYZ$ ; soient  $p, \varrho$  — la pression et la densité du liquide. J'admets que les forces extérieures n'existent pas, et pour simplifier, que la surface  $\Sigma$  possède partout une normale continue.

J'admets que les conditions suivantes sont satisfaites:

- (I) le liquide adhère à la surface  $\Sigma$ ; on aura donc sur cette surface  $u=v=0, w=W_0$ ;
- (II) l'énergie cinétique du mouvement est finie;
- (III) il existe une suite  $\{\pi_n\}$  de cylindres infiniment croissants à l'axe  $Z$  qui sont symétriques au plan  $XY$  et une constante  $M$  telle que

$$\iiint_{\pi_n} \varrho d\omega \leq M \iiint_{\pi_n} d\omega,$$

$$\iiint_{\pi_n} \frac{1}{\varrho} d\omega \leq M \iiint_{\pi_n} d\omega,$$

la moitié de la hauteur du cylindre  $\pi_n$  étant égale au carré de son rayon \*\*);

\*) Le mouvement plan d'un liquide visqueux et incompressible a été considéré par W. M. Wolibner [1], et celui du liquide compressible par l'auteur [2].

\*\*) Il suffit d'admettre que ces conditions sont remplies pour une suite encore plus spéciale de domaines.

(IV)  $u, v, w, p, \varrho$  et les dérivées de ces fonctions, qui apparaissent dans les équations du mouvement et dans celle de continuité sont continues \*).

Alors il existe deux suites de surfaces cylindriques  $\Phi_n$  et  $\Phi'_n$ , croissantes infiniment, telles que

$$(1) \quad \begin{aligned} P_x &= -\lim_n \left[ \int_{\Omega_n} \int \int \frac{\partial(\varrho u)}{\partial t} d\omega + R_n \int_{\Gamma_n} \int \frac{\partial(\varrho u_\varphi)}{\partial t} \sin \varphi d\sigma \right], \\ P_y &= -\lim_n \left[ \int_{\Omega'_n} \int \int \frac{\partial(\varrho v)}{\partial t} d\omega - R'_n \int_{\Gamma'_n} \int \frac{\partial(\varrho u_\varphi)}{\partial t} \cos \varphi d\sigma \right], \end{aligned}$$

$P_x$  et  $P_y$  désignant les composantes latérales de la force exercée sur l'obstacle par le liquide,  $u_\varphi$  ( $u_r$  et  $u_z$ ) — les composantes cylindriques de la vitesse absolue du liquide par rapport au système  $XYZ$ ,  $\Omega_n$  — le domaine contenu entre la surface  $\Sigma$  et la surface  $\Phi_n$ ,  $\Gamma_n$  — la surface latérale, et  $R_n$  — le rayon de la base de  $\Phi_n$ .

Si le mouvement est permanent par rapport au système  $XYZ$ , il résulte des formules (1) que le liquide n'exerce aucune force latérale sur la surface  $\Sigma$ .

Nous avons obtenu les formules (1) sans tenir compte de l'équation caractéristique du liquide comme dans le cas du mouvement plan du liquide. Ces formules ne résultent que des équations du mouvement et de l'équation de continuité; elles sont donc valables pour une fonction arbitraire  $p(x, y, z, t)$  et pour une vaste classe de mouvements, comme dans le cas du mouvement du liquide hétérogène, incompressible ou compressible, et même dans le cas où l'équation caractéristique du liquide dépend du temps.

La démonstration des formules (1) est analogue à celle utilisée dans le cas du mouvement plan du liquide [1], [2].

Les résultats communiqués dans la présente note seront publiés sous le même titre dans *Studia Mathematica*.

INSTITUT MATHÉMATIQUE DE L'ACADÉMIE POLONAISE DES SCIENCES

#### OUVRAGES CITÉS

[1] W. Wolibner, *Sur le mouvement plan du liquide visqueux incompressible, entourant une courbe simple fermée*, *Studia Math.* **12** (1951), 279.

[2] A. Krzywicki, *Sur le mouvement plan du liquide visqueux compressible*, *Studia Math.* (en préparation).

\*) Ces conditions et la condition concernant la surface  $\Sigma$  peuvent être affaiblies [1], [2].

# Sur quelques propriétés des fonctions définies sur des continus unicolhérents

par

K. HAMAN et K. KURATOWSKI

Présenté par K. KURATOWSKI le 23 Mars 1955

1. Introduction. Rappelons qu'un continu  $C$  est dit *unicolhérent*, lorsque pour toute décomposition  $C=A+B$  en deux continus le produit  $AB$  est connexe. Le continu  $C$  est dit *localement connexe* lorsqu'il est une image continue d'un intervalle (fermé). Dans la suite nous désignerons par  $C$  un continu unicolhérent et localement connexe (non vide) sur lequel on a défini une involution continue  $p^*$ , c'est-à-dire que

$$(1) \quad p^{**} = p.$$

Nous dirons que le point  $p^*$  est l'*antipode* du point  $p$  et nous appellerons *antipodique* tout ensemble  $X$  vérifiant l'égalité  $X^*=X$ , où  $X^*$  se compose de tous les points  $p^*$  tels que  $p \in X$ .

Nous allons établir le théorème suivant:

THÉORÈME 1. *Etant donnée une fonction continue  $f$  à valeurs réelles, définie sur  $C$ , l'ensemble  $F$  des points  $p$  de  $C$  tels que*

$$(2) \quad f(p) = f(p^*)$$

*contient un continu antipodique non vide.*

La sphère  $S_n$ , c'est-à-dire la surface de la boule à  $n+1$  dimensions, de centre 0 et de rayon 1, étant pour tout  $n > 1$  un continu unicolhérent localement connexe, on peut substituer dans le th. 1:  $C=S_n$  et  $p^*=-p$ .

Dans le cas particulier où  $C=S_2$  et  $p^*=-p$ , le théorème réciproque est vrai; plus précisément:

THÉORÈME 2 \*). *Etant donné sur  $S_2$  un ensemble fermé, antipodique  $F$  contenant un continu antipodique non vide  $K$ , il existe une fonction con-*

\*) Les théorèmes 1 et 2 répondent à un problème provenant de MM. G. Hajos et P. Alexandroff.

tinue  $f$  à valeurs réelles définie sur  $S_2$  et telle que  $F$  est l'ensemble des points  $p$  satisfaisant à la condition (2).

2. Démonstration du théorème 1. Nous allons baser notre démonstration sur le lemme suivant (établi dans la note [1], p. 117 et 118):

LEMME.  $A$  étant un sous-ensemble fermé antipodique de  $C$ , contenant un nombre fini de composantes\*), ou bien  $A$ , ou bien  $C-A$ , contient une composante antipodique.

A ce but, nous allons représenter l'ensemble  $F$  du th. 1 comme partie commune d'une suite descendante d'ensembles fermés antipodiques dont chacun contient un nombre fini de composantes:

$$(3) \quad F = F_1 \cdot F_2 \cdot \dots \cdot F_m \cdot \dots, \quad F_{m+1} \subset F_m, \quad F_m = F_m^*.$$

D'après un théorème général sur les continus localement connexes (cf. [2], p. 188), il existe une suite d'ensembles fermés  $H_1, H_2, \dots$ , dont chacun contient un nombre fini de composantes et telle que

$$F = H_1 \cdot H_2 \cdot \dots \cdot H_m \cdot \dots, \quad H_{m+1} \subset H_m.$$

En posant  $F_m = H_m + H_m^*$ , on constate facilement que les conditions (3) sont satisfaites et que l'ensemble  $F_m$  est antipodique et ne contient qu'un nombre fini de composantes. Pour en déduire (en vertu du lemme) que  $F_m$  contient une composante antipodique, il suffit donc de démontrer qu'aucune composante  $R$  de l'ensemble  $C - F_m$  n'est antipodique (dans l'hypothèse que  $F_m \neq C$ ).

Or, comme  $R \subset C - F_m \subset C - F$ , aucun point  $p$  de  $R$  ne vérifie l'égalité (2). Autrement dit, on a  $R = R_1 + R_2$ , où

$$R_1 = R \cdot \bigcup_p [f(p) < f(p^*)] \quad \text{et} \quad R_2 = R \cdot \bigcup_p [f(p) > f(p^*)].$$

Mais ceci est incompatible avec la connexité de l'ensemble  $R$  (non vide), car  $R_1^* = R_2$  (selon (1)), donc  $R_1$  et  $R_2$  sont deux ensembles non vides, ouverts et disjoints.

Il est ainsi établi que l'ensemble  $F_m$  contient une composante antipodique  $K_m$  (et que  $F_m \neq 0$ ). Il est légitime d'admettre que la suite  $K_1, K_2, \dots$  est convergente (car au besoin, on pourrait remplacer la suite  $F_1, F_2, \dots$  par une suite extraite convenable). Soit  $K$  sa limite. D'après (3)  $K \subset F$ . La limite d'une suite de continus antipodiques non vides étant un continu antipodique non vide, la démonstration du théorème se trouve achevée.

3. LEMME. Il n'existe, sur la sphère  $S_2$ , aucun couple de continus antipodiques disjoints et non vides.

\*) Par composante d'un ensemble  $A$  on entend un sous-ensemble connexe de  $A$  qui n'est contenu dans aucun autre sous-ensemble connexe de  $A$ .

Démonstration \*). Supposons, par contre, que  $A$  et  $B$  soient deux continus antipodiques disjoints et non vides. Soit  $R$  la composante de  $S_2 - A$  qui contient  $B$ . L'ensemble  $S_2 - A$  étant antipodique,  $R^*$  en est une composante et on a  $B^* \subset R^*$ . Comme  $B = B^* \neq 0$ , il vient  $R = R^*$  (les composantes étant disjointes).

Soit  $L$  un arc (ligne brisée) situé dans  $R$  et dont les extrémités (nommons les  $p$  et  $p^*$ ) sont antipodiques. Il est légitime d'admettre que l'arc  $L$  ne contient aucun couple de points antipodiques sauf les points  $p$  et  $p^*$ . Car, autrement, on désignerait par  $q$  le dernier point (sur l'arc  $L$  orienté de  $p$  à  $p^*$ ) suivi par son antipode sur  $L$ , et on n'aurait qu'à remplacer  $L$  par l'arc  $qq^*$ .

Cela étant, l'ensemble  $LL^*$  se réduit au couple  $(p, p^*)$ . En conséquence,  $L + L^*$  est une courbe simple fermée. Désignons par  $U$  et  $V$  les composantes de son complémentaire. Comme  $L + L^* \subset R \subset S_2 - A$  on a  $A \subset U + V$ . Soit

$$(4) \quad A \subset U, \text{ donc } AV = 0.$$

L'ensemble  $L + L^*$  étant antipodique, il en est de même de son complémentaire, c'est-à-dire de  $U + V$ . On a donc, soit  $U^* = U$ , soit  $U^* = V$ .

Le deuxième cas ne peut pas se présenter, car d'après (4) on a  $A^* \subset U^*$ , et comme  $A^* = A$ , il viendrait  $A \subset U^* = V$ , contrairement aux formules  $AV = 0$  et  $A \neq 0$ .

Nous parvenons ainsi à la conclusion que la région  $U$  est antipodique. Sa fermeture  $\bar{U} = U + L + L^*$  l'est donc également. La transformation  $\varphi(p) = p^*$  est donc une transformation continue de l'ensemble  $\bar{U}$  en lui-même sans point invariant. Mais, cela contredit le théorème de Brouwer puisque  $\bar{U}$  est homéomorphe au triangle (l'intérieur y compris).

Remarque. La démonstration reste valable dans l'hypothèse plus générale, que  $A$  est un continu et  $B$  un ensemble connexe (fermé ou non). Cependant le lemme est en défaut si l'on ne demande pas que l'un au moins des ensembles  $A$  ou  $B$  soit un continu. Pour s'en convaincre, envisageons deux courbes disjointes  $A$  et  $B$  situées dans l'hémisphère nord et approchant asymptotiquement l'équateur; soient sur l'équateur  $(p, p^*)$  et  $(q, q^*)$  deux couples de points disjoints. Les ensembles  $A + (p, p^*) + A^*$  et  $B + (q, q^*) + B^*$  sont connexes, antipodiques et disjoints.

4. Démonstration du théorème 2. Remarquons d'abord que l'ensemble  $S_2 - F$  ne contient aucune composante  $R$  antipodique. Car

\*) Ce lemme peut être déduit aussi d'un théorème d'Eilenberg, dont la démonstration est basée sur une idée différente (voir [3], théorème 4, p. 269). Un théorème établi récemment par J. Jaworowski [5], concernant les sphères  $S_n$  pour  $n$  arbitraire contient ce lemme comme cas particulier ( $n = 2$ ); sa démonstration est toutefois bien moins élémentaire.

dans le cas contraire, en unissant par un arc  $L$  dans  $R$  deux points antipodiques  $p$  et  $p^*$ , le continu  $L+L^*$  serait antipodique et disjoint du continu antipodique  $K$  (contrairement au lemme).

Il en résulte, qu'en désignant par  $R_1, R_2, \dots$  la suite (finie ou infinie) des composantes de  $S_2 - F$ , on a, pour tout  $k$ ,  $R_k^* \neq R_k$ , d'où  $R_k^* = R_{j_k}$  pour un  $j_k$  convenablement choisi et différent de  $k$ . Il est donc possible de numérotter les composantes de  $S_2 - F$  de façon que  $R_1^* = R_2$ ,  $R_2^* = R_4, \dots$

En posant  $G = R_1 + R_3 + R_5 + \dots$ , il vient  $S_2 - F = G + G^*$ . Soit \*)

$$f(p) = \begin{cases} \varrho(p, F) & \text{pour } p \in G + F, \\ -\varrho(p, F) & \text{pour } p \in G^* + F. \end{cases}$$

La fonction  $f$  est la fonction demandée.

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- [2] K. Kuratowski, *Topologie II*, Monogr. Mat. **21** (1950), Warszawa-Wrocław.
- [3] S. Eilenberg, *Sur quelques propriétés topologiques de la surface de sphère*, Fund. Math. **25** (1935), 267-272.
- [4] J. W. Jaworowski, *A theorem on antipodal sets on the  $n$ -sphere*, ce volume, p. 247.

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\*)  $\varrho(p, F)$  désigne l'écart du point  $p$  de l'ensemble  $F$ , c'est-à-dire la borne inférieure des distances de  $p$  à  $x$  où  $x \in F$ . C'est une fonction continue de  $p$ .

# A Theorem on Antipodal Sets on the $n$ -Sphere

by

J. W. JAWOROWSKI

Presented by K. BORSUK on March 23, 1955

1. Let  $S_n$  be the  $n$ -sphere defined in the  $n+1$ -dimensional Euclidean space  $E_{n+1}$  by the equation

$$x_1^2 + x_2^2 + \dots + x_{n+1}^2 = 1.$$

For every point  $x = (x_1, x_2, \dots, x_{n+1}) \in S_n$  the point  $\tilde{x} = (-x_1, -x_2, \dots, -x_{n+1})$  is called the *antipode* of  $x$ . If  $A \subset S_n$ , then by  $\tilde{A}$  we denote the set composed by all the points  $\tilde{x}$  with  $x \in A$ . The set  $A \subset S_n$  will be called *antipodal* if  $\tilde{A} = A$ .

We shall consider the chains and the cycles modulo 2 on  $S_n$ . By a  $p$ -dimensional simplex on  $S_n$  ( $p \geq 0$ ) we understand a set  $\sigma^p$  composed of  $p+1$  points of  $S_n$  with diameter  $< 1$ , called the vertices of  $\sigma^p$ . Linear independence of them will not be assumed. The  $p$ -dimensional chain  $\kappa^p$  modulo 2 on  $S_n$  may be considered as a set of a finite number of  $p$ -dimensional simplexes. We denote by  $\partial \kappa$  the boundary of the chain  $\kappa$ . By the boundary of a 0-dimensional simplex we shall understand the number 1 considered as a rest modulo 2. The rests 0 and 1 modulo 2 may be considered as  $(-1)$ -dimensional cycles. By the geometrical realization of a simplex  $\sigma$  we understand the smallest convex set on  $S_n$ \*) containing all the vertices of  $\sigma$ . The geometrical realization  $|\kappa|$  of a chain  $\kappa$  is assumed to be the sum of the geometrical realizations of all the simplexes belonging to  $\kappa$ .

We denote by  $\eta(\gamma^p, \delta^{n-p-1})$  the linking coefficient (see, e. g. [1], p. 416) of any two cycles  $\gamma^p$  and  $\delta^{n-p-1}$  on  $S_n$  with  $|\gamma^p| \cdot |\delta^{n-p-1}| = 0$ . Since in our case only chains modulo 2 are used, the values of  $\eta$  are 0 and 1. If  $p = -1$ , then  $\eta(\gamma^p, \delta^{n-p-1}) = 1$  if, and only if,  $\gamma^p = 1$ , and  $\delta^{n-p-1}$  is not homologous to zero on  $S_n$ .

For a chain  $\kappa$  on  $S_n$  by  $\tilde{\kappa}$  we denote the chain composed by all the simplexes  $\tilde{\sigma}$  with  $\sigma \in \kappa$ .

\*) We say that a subset  $E$  of  $S_n$  is convex, if for every two points  $a, b \in E$  the lesser of the arcs of the great circle passing through  $a$  and  $b$  lies in  $E$ .

By an *antipodal p-system* on  $S_n$  ( $-1 \leq p \leq n$ ) we shall understand a sequence of chains on  $S_n$

$$(\gamma^{-1}, \kappa^0, \gamma^0, \dots, \kappa^p, \gamma^p)$$

defined as follows:

$$1^0 \quad \gamma^{-1} = 1;$$

2<sup>0</sup> For some  $r$  ( $-1 \leq r < p$ ) let an  $r$ -dimensional cycle  $\gamma^r$  on  $S_n$  be already defined such that  $\hat{\gamma}^r = \gamma^r$ . Since  $r < n$ , the cycle  $\gamma^r$  is homologous to zero on  $S_n$ . Let  $\kappa^{r+1}$  be a chain on  $S_n$  such that

$$\partial \kappa^{r+1} = \gamma^r.$$

Then we put

$$\gamma^{r+1} = \kappa^{r+1} + \hat{\kappa}^{r+1}.$$

Thus  $\gamma^{r+1}$  is an  $(r+1)$ -dimensional cycle on  $S_n$  and  $\hat{\gamma}^{r+1} = \gamma^{r+1}$ .

Let  $M$  be a compact metric space. We shall consider the homology theory of  $M$  in the sense of Vietoris [2]. Thus a true chain of  $M$  is a sequence  $\underline{\kappa} = \{\kappa_i\}$ ,  $\kappa_i$  being a chain composed of the simplexes (considered as finite subsets of  $M$ ) and such that the maximum of the diameters of the simplexes of  $\kappa_i$  tend to zero if  $i$  tends to  $\infty$ . A true chain  $\underline{\gamma} = \{\gamma_i\}$  is called a true cycle, if  $\partial \underline{\gamma} = \{\partial \gamma_i\} = 0$ . A  $p$ -dimensional true cycle  $\underline{\gamma}^p$  is said to be homologous to zero in  $M$  if there exists in  $M$  a true  $(p+1)$ -dimensional chain  $\underline{\kappa}^{p+1}$  such that  $\partial \underline{\kappa}^{p+1} = \underline{\gamma}^p$ . The space  $M$  is said to be *p-acyclic* if every  $(r-1)$ -dimensional true cycle with  $-1 \leq r \leq p$  is homologous to zero in  $M$ . For instance,  $S_n$  is  $n$ -acyclic but not  $(n+1)$ -acyclic.

Let us suppose that  $A$  and  $B$  are two disjoint closed subsets of  $S_n$  and let  $\underline{\gamma} = \{\gamma_i\}$  be a true  $p$ -dimensional cycle of  $A$  and  $\underline{\delta} = \{\delta_i\}$  — a true  $(n-p-1)$ -dimensional cycle of  $B$ . Then, for almost all indices  $i$  and  $j$ ,  $|\gamma_i| \cdot |\delta_j| = 0$ . If for almost all  $i$  and  $j$   $\eta(\gamma_i, \delta_j) = 1$ , then the cycles  $\underline{\gamma}$  and  $\underline{\delta}$  are said to be *linked modulo 2*. If, for some  $p$ , there exists a  $p$ -dimensional true cycle  $\underline{\gamma}$  in  $A$ , and an  $(n-p-1)$ -dimensional true cycle  $\underline{\delta}$  in  $B$ , such that the cycles  $\underline{\gamma}$  and  $\underline{\delta}$  are linked modulo 2, then we say, that the sets  $A$  and  $B$  are *linked modulo 2*.

Let now  $M$  be a closed antipodal subset of  $S_n$ . If  $M$  is  $p$ -acyclic, we can construct in  $M$  a *true antipodal p-system*

$$(\underline{\gamma}^{-1}, \underline{\kappa}^0, \underline{\gamma}^0, \dots, \underline{\kappa}^p, \underline{\gamma}^p)$$

which is a sequence of true chains of  $M$  such that

$$1^0 \quad \underline{\gamma}^{-1} = 1$$

2<sup>0</sup>  $\underline{\kappa}^{r+1}$ , for  $-1 \leq r < p$ , is a true chain of  $M$  with  $\partial \underline{\kappa}^{r+1} = \underline{\gamma}^r$ . Finally we put

$$\underline{\gamma}^{r+1} = \underline{\kappa}^{r+1} + \hat{\underline{\kappa}}^{r+1}.$$

2. The purpose of this note is to give the idea of the proof of the following

**THEOREM.** *Let  $A$  and  $B$  be two antipodal and closed subsets of  $S_n$  such that  $A$  is  $p$ -acyclic and  $B$  is  $(n-p-1)$ -acyclic. Let  $(\gamma^{-1}, \underline{\kappa}^0, \gamma^0, \dots, \underline{\kappa}^p, \gamma^p)$  be a true antipodal  $p$ -system in  $A$  and  $(\delta^{-1}, \underline{\lambda}^0, \delta^0, \dots, \underline{\lambda}^{n-p-1}, \delta^{n-p-1})$  — a true antipodal  $(n-p-1)$ -system in  $B$ . Then, if  $A \cdot B = 0$ , the true cycles  $\underline{\gamma}^p$  and  $\underline{\delta}^{n-p-1}$  are linked modulo 2.*

From this theorem we obtain the following

**COROLLARY 1.** *Let  $A$  and  $B$  be two closed antipodal and disjoint subsets of  $S_n$  such that  $A$  is  $p$ -acyclic and  $B$  is  $(n-p-1)$ -acyclic. Then  $A$  and  $B$  are linked modulo 2.*

Thus, for instance, two disjoint great spheres  $S'_p$  and  $S''_{n-p-1}$  on  $S_n$ , of dimensions  $p$  and  $n-p-1$ , respectively, are linked modulo 2; this fact can be verified immediately. Furthermore, two disjoint antipodal continua on  $S_3$  are linked modulo 2. A closed antipodal  $(n-1)$ -acyclic subset of  $S_n$  disconnects  $S_n$  between every antipodal pair of points of its complement.

**COROLLARY 2.** *Let  $A$  and  $B$  be two antipodal and closed subsets of  $S_n$  such that  $A$  is  $p$ -acyclic and  $B$  is  $q$ -acyclic with  $p+q > n-1$ . Then  $A \cdot B \neq 0$ .*

For, if we suppose that  $A \cdot B = 0$ , the assumption of the theorem will be fulfilled. But  $q > n-p-1$  and consequently the cycle  $\delta^{n-p-1}$  is homologous to zero in  $B$ . It follows that the cycles  $\underline{\gamma}^p$  and  $\underline{\delta}^{n-p-1}$  were not linked.

Thus, for instance, two antipodal continua on  $S_2$  have common points (see [3], theorem 4, p. 269, and [4], N° 2, lemma, p. 243).

3. The proof of the theorem is based on two lemmas:

**LEMMA 1.** *Let  $(\gamma^{-1}, \kappa^0, \gamma^0, \dots, \kappa^n, \gamma^n)$  be an antipodal  $n$ -system on  $S_n$ . Then the cycle  $\gamma^n$  is not homologous to zero on  $S_n$ .*

The proof of this lemma is by induction with respect to  $n$ .

**LEMMA 2.** *If  $(\gamma^{-1}, \kappa^0, \gamma^0, \dots, \kappa^p, \gamma^p)$  is an antipodal  $p$ -system and  $(\delta^{-1}, \lambda^0, \delta^0, \dots, \lambda^{n-p-1}, \delta^{n-p-1})$  — an antipodal  $(n-p-1)$ -system on  $S_n$  such that  $\sum_{r=0}^p (|\kappa^r| + |\tilde{\kappa}^r|) \cdot \sum_{s=0}^{n-p-1} |\lambda^s| = 0$ , then  $\eta(\gamma^p, \delta^{n-p-1}) = 1$ .*

The proof is by induction with respect to  $p$ . The first step of the induction is stated in lemma 1.

Now we shall prove the theorem. Let  $\gamma^r = \{\gamma_i^r\}$ ,  $\underline{\kappa}^r = \{\kappa_i^r\}$ ,  $\underline{\delta}^s = \{\delta_i^s\}$ ,  $\underline{\lambda}^s = \{\lambda_i^s\}$ . Thus  $(\gamma_i^{-1}, \kappa_i^0, \gamma_i^0, \dots, \kappa_i^p, \gamma_i^p)$  is an antipodal  $p$ -system and  $(\delta_j^{-1}, \lambda_j^0, \delta_j^0, \dots, \lambda_j^{n-p-1}, \delta_j^{n-p-1})$  — an antipodal  $(n-p-1)$ -system on  $S_n$ . Since  $A \cdot B = 0$ , the condition  $\sum_{r=0}^p (\kappa_i^r + \tilde{\kappa}_i^r) \cdot \sum_{s=0}^{n-p-1} \lambda_j^s = 0$  will be satisfied for almost

all  $i$  and  $j$ . Therefore, by lemma 2,  $\eta(\gamma_i^p, \delta_j^{n-p-1}) = 1$  for almost all indices  $i$  and  $j$ , and, consequently, the true cycles  $\gamma^p$  and  $\delta^{n-p-1}$  are linked modulo 2.

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# Sur la notion de dépendance des transformations continues

par

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Présenté le 23 Mars 1955

1. Considérons l'espace  $Y_0^{X_0}$  des transformations continues d'un espace compact  $X_0$  en sous-ensembles d'un espace compact  $Y_0$  supposé *ANR*, tout comme nous l'avons fait dans la communication précédente [1]. Pour tout  $f \in Y_0^{X_0}$ , désignons par  $(f)$  la *classe d'homotopie* de  $f$ , c'est-à-dire la composante de l'espace  $Y_0^{X_0}$  contenant la fonction  $f$ .

Nous dirons qu'une fonction  $g \in Y_0^{X_0}$  *dépend* d'un ensemble de fonctions  $\Phi \subset Y_0^{X_0}$  lorsque, pour tout espace compact  $X \supset X_0$ , l'existence des prolongements sur  $X$  (continus et ayant leurs valeurs dans  $Y_0$ ) de toutes les fonctions  $f \in \Phi$  implique celle d'un prolongement sur  $X$  de la fonction  $g$ . L'ensemble de toutes les fonctions  $g \in Y_0^{X_0}$  dépendant de  $\Phi$  sera désigné par  $\mathfrak{R}(\Phi)$ . Dans le cas où  $\Phi$  n'est qu'un ensemble fini de fonctions  $f_1, f_2, \dots, f_k$ , nous désignerons  $\mathfrak{R}(\Phi)$  aussi par  $\mathfrak{R}(f_1, f_2, \dots, f_k)$ .

Il est clair que  $f \in \mathfrak{R}(\Phi)$  entraîne  $(f) \subset \mathfrak{R}(\Phi)$ . D'autre part,  $(\Phi)$  désignant l'union de toutes les classes  $(f)$  où  $f \in \Phi$ , on a  $\mathfrak{R}(\Phi) = \mathfrak{R}((\Phi))$ . Par conséquent, la dépendance  $g \in \mathfrak{R}(\Phi)$  est en réalité une relation entre la classe  $(g)$  et les classes  $(f)$  des fonctions  $f \in \Phi$ .

Evidemment  $\mathfrak{R}(0)$  coïncide avec l'ensemble de toutes les *zéro-fonctions*, c'est-à-dire des fonctions homotopes à des constantes, et  $\mathfrak{R}(f_1)$  coïncide avec celui de tous les *multiples* de  $f_1$  (voir [1]).

On a en outre

$$\begin{aligned}\Phi \subset \mathfrak{R}(\Phi) &= \mathfrak{R}[\mathfrak{R}(\Phi)], \\ \mathfrak{R}(\Phi_1 \cup \Phi_2) &\supset \mathfrak{R}(\Phi_1) \cup \mathfrak{R}(\Phi_2), \\ \mathfrak{R}(\Phi_1 \cap \Phi_2) &\subset \mathfrak{R}(\Phi_1) \cap \mathfrak{R}(\Phi_2).\end{aligned}$$

EXEMPLE. Lorsque  $Y_0$  est un groupe topologique, l'espace  $Y_0^{X_0}$  l'est aussi. Dans ce cas, l'ensemble  $\mathfrak{R}(\Phi)$  est un sous-groupe de  $Y_0^{X_0}$  contenant en particulier toutes les fonctions de la forme  $\psi f$  où  $\psi \in Y_0^{X_0}$  et où  $f$  appartient au sous-groupe de  $Y_0^{X_0}$  engendré par  $\Phi$ .

2. Nous dirons qu'une fonction  $g \in Y_0^{X_0}$  dépend d'un ensemble  $\Phi \subset Y_0^X$  en dimension  $m$  lorsque, pour tout espace compact  $X \supset X_0$  satisfaisant à la condition  $\dim(X - X_0) \leq m$ , la prolongeabilité de toute fonction  $f \in \Phi$  sur  $X$  entraîne celle de  $g$  sur  $X$ . L'ensemble de toutes les fonctions qui dépendent de  $\Phi$  en dimension  $m$  sera désignée par  $\mathfrak{R}_m(\Phi)$ . Lorsque  $\Phi$  n'est qu'un ensemble fini de fonctions  $f_1, f_2, \dots, f_k$ , l'ensemble  $\mathfrak{R}_m(\Phi)$  sera aussi désigné par  $\mathfrak{R}_m(f_1, f_2, \dots, f_k)$ . Tout comme la dépendance  $g \in \mathfrak{R}(\Phi)$ , la dépendance  $g \in \mathfrak{R}_m(\Phi)$  en dimension  $m$  est en réalité une relation entre la classe  $(g)$  et les classes  $(f)$  des fonctions  $f \in \Phi$ .

$\mathfrak{R}_m(0)$  coïncide avec l'ensemble des fonctions dites *zéro-fonctions en dimension  $m$*  (voir [1]) et  $\mathfrak{R}_m(f_1)$  coïncide avec celui des fonctions dites *multiples en dimension  $m$  de  $f_1$*  (voir [1]).

On a en outre

$$\begin{aligned}\Phi \subset \mathfrak{R}_m(\Phi) &= \mathfrak{R}_m[\mathfrak{R}_m(\Phi)], \\ \mathfrak{R}_m(\Phi_1 \cup \Phi_2) &\supset \mathfrak{R}_m(\Phi_1) \cup \mathfrak{R}_m(\Phi_2), \\ \mathfrak{R}_m(\Phi_1 \cap \Phi_2) &\subset \mathfrak{R}_m(\Phi_1) \cap \mathfrak{R}_m(\Phi_2), \\ \mathfrak{R}(\Phi) &\subset \mathfrak{R}_{m+m'}(\Phi) \subset \mathfrak{R}_m(\Phi) \quad \text{pour } m, m' = 0, 1, \dots\end{aligned}$$

PROBLÈME 1. Est-ce que  $\mathfrak{R}(\Phi) = \mathfrak{R}_{m+1}(\Phi)$  lorsque  $m = \dim X_0$ ?

3. Le problème de trouver les conditions nécessaires et suffisantes pour qu'une fonction  $g \in Y_0^{X_0}$  dépende (ou dépende en dimension  $m$ ) d'un ensemble de fonctions  $\Phi \subset Y_0^X$  ne se laisse actuellement résoudre que dans quelques cas spéciaux. Dans le cas classique de Hopf, qui est celui dans lequel  $\dim X_0 \leq n$  et  $Y_0$  est une sphère euclidienne de dimension  $n$ , les classes d'homotopie constituent un groupe abélien connu sous le nom de *groupe de Hopf* de l'espace  $X_0$  (voir [4]); l'addition y fait correspondre aux classes  $(f_1), (f_2) \subset Y_0^{X_0}$  une classe  $(f_3) \subset Y_0^{X_0}$  telle qu'on a  $f_1(\gamma) + f_2(\gamma) \sim f_3(\gamma)$  dans  $Y_0$  pour tout vrai cycle  $\gamma$  situé dans  $X_0$ .

Dans le cas de Hopf, on a le théorème suivant:

THÉORÈME. Soient:  $X_0$  un espace compact,  $\dim X_0 \leq n$ ,  $Y_0$  une sphère euclidienne de dimension  $n$ ,  $m$  un entier,  $n < m < 2n$  et  $f_1, f_2, \dots, f_k$  des fonctions appartenant à  $Y_0^{X_0}$ . Alors la classe  $\mathfrak{R}_m(f_1, f_2, \dots, f_k)$  est le sous-groupe du groupe de Hopf de  $X_0$  engendré par les classes d'homotopie  $(f_1), (f_2), \dots, (f_k)$ .

La démonstration s'appuie sur deux lemmes qui suivent.

LEMME 1. Soit  $f_1, f_2, \dots, f_k$  un système de fonctions continues transformant un espace compact  $X_0$  où  $\dim X_0 \leq n$  en une sphère euclidienne  $Y_0$  de dimension  $n$ . Pour tout point  $y_0 \in Y_0$ , il existe un système de fonctions  $g_1, g_2, \dots, g_k \in Y_0^{X_0}$  homotopes respectivement aux fonctions  $f_1, f_2, \dots, f_k$  et assujetties à la condition suivante:

(\*) Les ensembles  $G_i = g_i^{-1}(Y_0 - (y_0))$ , où  $i = 1, 2, \dots, k$ , sont disjoints deux à deux.

La démonstration de ce lemme, connu dans le cas particulier où  $k=2$  (voir [3] p. 735 et [5] p. 209), est tout à fait élémentaire.

Les fonctions  $g_1, g_2, \dots, g_k \in Y_0^{X_0}$  assujetties à (\*) seront dites *séparées*. La thèse du lemme 1 peut donc être formulée aussi comme suit: *dans le cas de Hopf il existe pour tout système de fonctions  $f_1, f_2, \dots, f_k \in Y_0^{X_0}$  un système de fonctions séparées  $g_1, g_2, \dots, g_k \in Y_0^{X_0}$  qui leur sont respectivement homotopes.*

En posant

$$g(x) = \begin{cases} g_i(x) & \text{pour } x \in G_i \text{ où } i=1, 2, \dots, k, \\ y_0 & \text{pour } x \in X_0 - \bigcup_{i=1}^k G_i, \end{cases}$$

on obtient une fonction  $g \in Y_0^{X_0}$ . Nous dirons que toute fonction  $f \in Y_0^{X_0}$  homotope à une fonction  $g \in Y_0^{X_0}$  obtenue de cette manière est une *somme homotopique* des fonctions  $f_1, f_2, \dots, f_k$ .

LEMME 2. *Dans les hypothèses du lemme 1, la classe  $\mathfrak{R}_m(f_1, f_2, \dots, f_k)$  coïncide avec l'union de toutes les classes d'homotopie des fonctions qui sont les sommes homotopiques des multiples de fonctions  $f_1, f_2, \dots, f_k$ .*

La démonstration de ce lemme est basée sur la notion de cylindre d'homotopie de J. H. C. Whitehead (voir [6] p. 259).

On démontre aisément que dans le cas où l'espace  $Y_0$  est connexe, toute fonction  $f$  qui est la somme homotopique des fonctions  $f_1, f_2, \dots, f_k \in Y_0^{X_0}$  transforme tout vrai cycle  $\gamma$  situé dans  $X_0$  en un vrai cycle  $f(\gamma)$  homologue dans  $Y_0$  à la somme des cycles  $f_1(\gamma), f_2(\gamma), \dots, f_k(\gamma)$ . Il en résulte d'après le lemme 2 que, dans les hypothèses de ce lemme, la classe  $\mathfrak{R}_m(f_1, f_2, \dots, f_k)$  coïncide avec la combinaison linéaire

$$\lambda_1(f_1) + \lambda_2(f_2) + \dots + \lambda_k(f_k),$$

où  $\lambda_1, \lambda_2, \dots, \lambda_k$  sont des entiers et combinaison linéaire est entendue dans le sens du groupe de Hopf de  $X_0$ . Or on obtient ainsi la thèse de notre théorème.

4. La notion de dépendance des transformations permet de faire correspondre aux espaces  $X_0$  et  $Y_0$  un nombre entier de la manière analogue que la notion de groupe de Betti conduit au nombre de Betti. Nous dirons qu'un système de fonctions  $f_1, f_2, \dots, f_k \in Y_0^{X_0}$  est *indépendant* lorsque aucune d'elles ne dépend de l'ensemble des autres. Appelons la borne supérieure des puissances des tous les systèmes indépendants contenus dans  $Y_0^{X_0}$  l'index  $J(X_0, Y_0)$ ; il correspond donc au couple des espaces  $X_0$  et  $Y_0$ . Dans le cas de Hopf, l'index est déterminé par les propriétés d'homologie de l'espace  $X_0$ . En particulier, il est fini dans le cas de Hopf lorsque  $X_0$  est un polytope.

PROBLÈME 2. *Est-ce que l'index  $J(X_0, Y_0)$  est toujours fini lorsque  $X_0$  et  $Y_0$  sont des polytopes?*

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# On a Group-Theoretical Systematization of Elementary Particles

by

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*Presented by L. INFELD on March 23, 1955*

The proposed systematization is based on the following idea: matter must not be an intruder in space-time, but both should be very intimately connected with each other. A close connection between them will be secured by the following postulate: to every irreducible representation (single or double valued) of the group of rotations and reflections in space there should correspond (at least) one particle type. Thus, we may classify the types of elementary particles according to representations of the unitary unimodular group, i. e. according to spin  $0, \frac{1}{2}, 1, \frac{3}{2}, \dots$  and according to reflection symmetry (parity). Since the particles may be described either by the first or the second order wave equation (Dirac, Kemmer, or Schrödinger-Gordon equations) for both integral and half-integral spin, we have to expect that the correspondence between possible particle types and irreducible representations is not unique: to every representation there should correspond two particle types.

The possible sorts of particles are arranged into families in the following table. We notice the existence of two tensor and two pseudo-tensor families for bosons, and six families of spinors according to the types of symmetry against inversions of space axes

$$(1) \quad \psi' = x\gamma^4\psi,$$

where  $x$  is either  $\pm$  or  $\mp$  or  $\pm i$  or  $\mp i$ . The difference between  $\pm$  and  $\mp$  has only a relative meaning. We distinguish only two but not four families of the type  $\pm$  since the reversed cases ( $\mp$ ) are realized by the respective antiparticles.

We notice the following absolute selection rules: nucleons and hyperons cannot decay into lighter fermions,  $\tau$  cannot decay into two pions. There exist other selection rules favouring the processes

$$Y \rightarrow A + \pi, \quad F \rightarrow N + \pi \text{ (or } \tau), \quad \pi \rightarrow \mu + \nu, \quad K_e \rightarrow e + \nu + \nu, \quad K_\mu \rightarrow \mu + \nu + \nu, \\ \bar{\mu} + P \rightarrow N + \nu,$$

(as compared with the alternatives  $Y \rightarrow N + \pi$ ,  $F \rightarrow \Lambda + \pi$ ,  $\pi \rightarrow e + \nu$ ,  $K_e \rightarrow \mu + \nu + \nu$ ,  $K_\mu \rightarrow e + \nu + \nu$ ,  $\bar{\mu} + P \rightarrow P + e$ ) in agreement with the experimental evidence.

Table I

I-st order				bosons				II-nd order							
spin	0	1	2	s.	0	1	2	s.	0	1	2	s.	0	1	2
parity	-	+	-	p.	+	-	+	p.	-	+	-	p.	+	-	+
name	$\bar{\eta}$	$\eta$	$\eta$	n.	$\theta$	$\eta$	$\eta$	n.	$\pi$	$\eta$	$\eta$	n.	$\eta$	$\eta$	$\eta$

fermions																									
s.				$1/2$	$3/2$				$5/2$				s.				$1/2$	$3/2$				$5/2$			
p.				$\pm$	$\mp$				$\pm$				p.				$\mp$	$\pm$				$\mp$			
n.				$P, N$	$Y^-$				$\eta$				n.				$X$	$\Lambda^0, \Omega^\pm$				$F^{0+}$			

s.				$1/2$	$3/2$				$5/2$				s.				$1/2$	$3/2$				$5/2$			
p.				$\pm i$	$\mp i$				$\pm i$				p.				$\mp i$	$\pm i$				$\mp i$			
n.				$K^0$	$\eta$				$\eta$				n.				$e$	$K_e$				$\eta$			

s.				$1/2$	$3/2$				$5/2$				s.				$1/2$	$3/2$				$5/2$			
p.				$\mp i$	$\pm i$				$\mp i$				p.				$\pm i$	$\mp i$				$\pm i$			
n.				$\nu, \mu$	$K_\mu$				$\eta$				n.				$\nu, \mu$	$K_\mu$				$\eta$			

A two-coupling-constants hypothesis enables to explain long life times, copious production of pairs of heavy particles, and the share of hyperons in nuclear forces.

The whole family of particles with higher spins may be conveniently described by a bilocal field quantity  $\psi(x, r)$  restricted by two Born-invariant supplementary conditions \*). It may be shown that the bilocal field quantity is a generating function for the (local) fields with higher spins

$$(2) \quad \psi(x, r) = \psi(x) + r_\mu \psi(x)_\mu + r_\mu r_\nu \psi(x)_{\mu\nu} + \dots,$$

which establishes a connection with the formalism of Fierz. The bilocal formalism yields the following formulae for the mass spectra

$$(3) \quad M_n = \frac{C}{l} \sqrt{n+1}, \quad M_n = \frac{C}{l} \sqrt{n(n+1)}$$

for the cases of the I-st and II-nd order field equations respectively. The spin of the particle in question is  $n$  for bosons and  $n+1/2$  for fermions;  $l$  denotes a fundamental length while  $C$  is a dimensionless constant. The theoretical mass values for neutrino, electron, muon, and pion are simply zero which should be interpreted as follows: these particles possess no mechanical masses but only self-masses brought about by the interaction. We have to exclude (by a special assumption) the

\*) Details will be published in Acta Phys. Pol. 14 (1955).

lowest member of the  $\Lambda^0$ -family (i. e. in this case  $n=1,2,\dots$ ). Adjusting the constant  $C$  from the mass value of the nucleon, we get from (3) the value 2597 for the cascade hyperon  $Y$  and (with the same  $C$ ) the values 2185 and 2860 for the hyperons  $\Lambda^0$  and  $F$ . These values are confirmed by experimental results. The difference between the mass values of  $\Omega^\pm$  and  $\Lambda^0$  as well as that between muon and neutrino may be regarded as of electromagnetic origin.

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## Sur les spectres ramanien de la pyridine dans les mélanges avec l'acide acétique

par

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*Présenté par A. SOLTAN le 28 Février, 1955*

**Introduction.** Dans les mélanges liquides les molécules de chaque substance composante exercent généralement une influence sur celles des autres substances composantes. On ne sait pas actuellement exactement quelle est cette influence, mais on admet qu'elle a un effet sur les oscillations des atomes dans les molécules et, par conséquent, sur les spectres d'oscillation. Les recherches présentes qui font une suite d'études des fréquences des raies ramanien de la pyridine dans des mélanges avec l'acide acétique de différentes concentrations, indiquent que par l'étude des spectres ramanien on parvient à certains résultats qui peuvent être intéressants au point de vue de ce problème difficile.

**Appareillage.** Le mode de préparation, de déshydratation, ainsi que d'analyse des mélanges et les conditions de la pose ont été décrites dans [1]. La détermination des fréquences des raies ramanien a été basée sur les mesures de leur position relative aux raies Hg 4313 Å et 4916 Å (au lieu des raies 4343 Å et 4916 Å dans [1], car la raie 4343 Å était trop faible). Cela nous a permis d'atteindre une plus grande précision, ainsi qu'une exactitude relative plus élevée des fréquences mesurées. Pour les raies nettes les erreurs relatives ne dépassent pas 0.3 K \*) pour les mélanges de différentes concentrations. Le degré d'exactitude des mesures dans [1] était exagéré. Les fréquences des raies dans les spectres de la pyridine et des mélanges ont été mesurées de nouveau.

On a préparé des mélanges de pyridine et d'acide acétique contenant 91.5, 80.8, 73.2, 61.0, 48.3, 43.3, 39.8, 37.8, 30.4, 22.3, 21.6, 14.6 et 6.5% de pyridine par mole. La variété des mélanges de différentes concentrations, plus grande que dans [1], a permis une meilleure corrélation des raies des mélanges avec celles des substances pures.

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\*) 1 K (kayser) =  $1 \text{ cm}^{-1}$ . d'après la proposition acceptée en 1952 par la Commission Internationale de la Spectrographie.

Dans le communiqué présent sont décrits les changements des fréquences des raies de la pyridine dans les mélanges avec l'acide acétique. Le communiqué suivant [2] donne les déplacements des raies de l'acide acétique dans les mêmes mélanges.

**Résultats.** Dans les spectres des mélanges on a constaté l'apparition de raies nouvelles qui n'apparaissent pas dans les spectres des substances pures. La raie de fréquence 1002 K, qui avait été déjà annoncée auparavant [1], apparaît dans les spectres des mélanges conte-

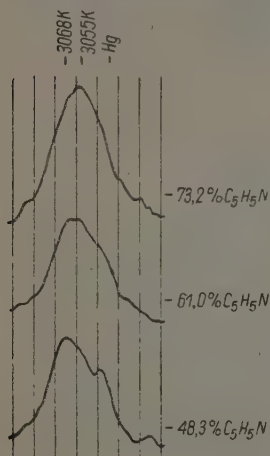


Fig. 1.

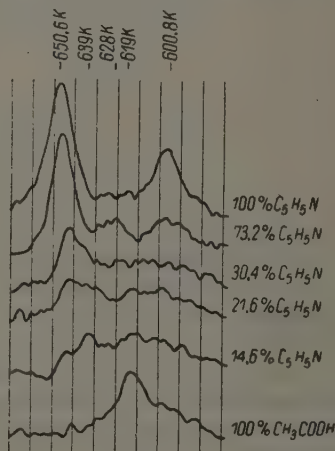


Fig. 2.

nant au-dessous de 10% de l'acide par mole. La raie de fréquence 3068.5 K est décélable dans les spectres des mélanges contenant moins de 30% d'acide. La fréquence de cette raie est très proche à la fréquence de la raie de pyridine 3055.5 K et comme les deux dernières sont assez larges, elles forment une bande commune. On ne peut les distinguer que par les variations de la courbe photométrique des spectres des mélanges de différentes concentrations (Fig. 1). Dans [1] on a remarqué un déplacement considérable de cette raie. Il semble, que ce déplacement peut être maintenant expliqué comme étant le résultat des changements des intensités des raies 3055.5 et 3068.5 K par rapport à la concentration.

La raie nouvelle de fréquence 628 K environ (Fig. 2) est observée dans les spectres des mélanges contenant moins de 80% de pyridine; dans celles qui contiennent moins de 38% de cette substance elle ne peut pas être décélée. Comme le montrent les courbes photométriques dans les spectres des ces mélanges on observe une raie de fréquence 639 K environ.

L'existence de la raie 1019 K, qui était annoncée dans [1] comme probable, est confirmée dans les études plus récentes. Son intensité aug-

mente dans les spectres des mélanges étudiés à mesure que la concentration de la pyridine décroît.

Dans [1] on a signalé des changements caractéristiques des spectres dans la région vers 1600 K. Au lieu de trois raies de pyridine: deux de fréquences 1572.7 K et 1580 K d'intensité moyenne, et une faible raie de fréquence 1595.8 K — on observe dans les spectres des mélanges deux raies de fréquences 1574.1 K et 1595.3 K d'intensité égale. Comme on le voit à la figure 3 c'est la raie 1580 K, qui disparaît rapidement dans les spectres quand la concentration de la pyridine décroît.

Les résultats des mesures des fréquences de quelques raies de pyridine sont rassemblés dans le tableau 1. On a marqué par + les raies pour lesquelles les résultats des mesures ne sont pas assez précis. En examinant le tableau 1 on constate des déplacements continus de fréquences à mesure qu'on change la concentration de la pyridine d'accord avec [1]. Les profils des raies 650.6, 989.4, 1002 et 1028.5 sont symétriques et on ne peut pas même découvrir de traces de raies nouvelles à leurs ailes.

On peut alors admettre que les déplacements de ces raies sont continus et on ne peut pas les expliquer (comme ont essayé de la faire Joerges

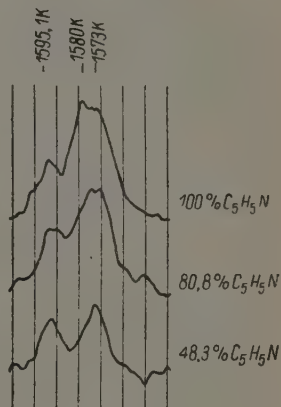


Fig. 3.

TABLEAU I

% mole C <sub>5</sub> H <sub>5</sub> N													
100	91.5	80.8	73.2	61.0	48.3	43.3	39.8	37.8	30.4	22.3	21.6	14.6	6.5
600.8	600.8	+	+	+	+	—	—	—	—	—	—	—	—
—	—	(628)	+	+	+	+	+	+	—	—	—	—	—
—	—	—	—	—	—	—	—	—	(639)	+	+	+	+
650.6	650.6	650.5	650.1	649.9	649.7	649.7	649.7	649.7	649.7	+	—	—	—
888.3	+	+	+	—	—	—	—	—	—	—	—	—	—
989.4	989.4	989.4	989.4	989.5	989.5	989.7	989.9	+	+	+	—	—	—
—	1001.8	1002.6	1002.6	1002.6	1002.8	1003.1	1003.1	1003.2	1004.9	1005.9	1006.2	1006.9	1007.3
—	—	—	—	—	—	—	—	—	—	+	—	1019.0	1020.6
1028.5	1028.5	1028.6	1028.8	1029.3	1029.9	1030.3	1030.7	1030.8	1031.5	1032.4	1032.9	+	—
1215.6	1215.3	1215.4	1214.5	1214.4	1213.2	1213.2	1213.5	1212.3	+	—	—	—	—
1572.7	1572.7	1572.7	1573.0	1573.5	1574.1	1574.1	1574.1	1574.1	+	+	+	—	—
1580	+	+	+	+	—	—	—	—	—	—	—	—	—
1595.8	1595.3	1595.3	1595.3	1595.3	1595.3	1595.6	1595.6	1595.8	+	+	—	—	—
3055.4	3055.9	3056.8	3057.8	3058.2	—	—	—	—	—	—	—	—	—
—	—	—	—	+	3068.5	3068.5	3068.5	3068.5	3068.5	+	+	+	—

et Nikuradsé [3] au cours des études des autres mélanges) par changement de l'intensité des raies caractéristiques pour les mélanges de différentes concentrations (contrairement à ce qu'on observe dans le cas de la raie 3055.5 K).

**Conclusions.** Les raies de fréquences 628, 1002 et 3068.5 K peuvent apparaître comme conséquence de la formation d'un complexe de molécules de la pyridine et de l'acide acétique comme nous l'avions supposé dans [1]. Une raie de fréquence 1008 K environ qui a été trouvée dernièrement par Tramer [4] dans les spectres ramanien des mélanges de la pyridine et de  $\text{SO}_2$ , peut aussi confirmer cette supposition. La fréquence de la raie 639 K est assez proche de la fréquence 638 K trouvée par Bernstein et Martin [5] dans les spectres ramanien de la pyridine avec de l'acide chlorhydrique. L'apparition de cette raie dans les mélanges étudiés peut indiquer que dans les mélanges de pyridine avec l'acide acétique contenant au-dessous de 30% de pyridine, existent aussi des ions de  $(\text{C}_5\text{H}_5\text{NH})^+$ . Il se peut que la raie 1019 K soit analogue à celle de fréquence 1013 K trouvée par Bernstein et Martin [5] ou bien identique avec une raie faible de l'acide acétique de fréquence 1020 K [6] qui, dans nos conditions, n'est pas décélable dans les spectres de la substance pure.

Les déplacements continus des raies de la pyridine peuvent être l'effet de l'influence des molécules de l'acide acétique sur les molécules de pyridine. Cette influence semble dépendre du nombre de molécules de l'acide qui se trouvent autour de chaque molécule de pyridine. Il est possible que ce soient les moments dipolaires de molécules de l'acide et de la pyridine qui sont responsables de cette influence.

Les mesures d'intensité des raies nouvelles qui sont actuellement en cours permettront de poursuivre l'étude de la constitution des complexes intermoléculaires se formant dans les mélanges de la pyridine et de l'acide acétique.

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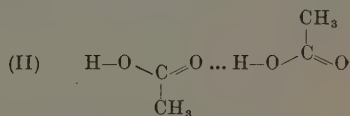
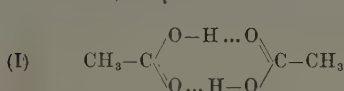
# Sur les spectres ramanien de l'acide acétique dans des mélanges avec la pyridine

par

R. MIERZECKI

*Présenté par A. SOŁTAN le 28 Février 1955*

**Introduction.** On sait que les molécules de l'acide acétique forment dans la substance pure liquide des dimères. Chaque molécule peut être liée à une autre soit par deux liaisons hydrogénées, soit par une seule. Dans le premier cas le dimère prend la forme d'un noyau (I), dans le second, celle d'une chaîne (II).



En examinant les spectres ramanien des solutions aqueuses de l'acide acétique, Suzanne Fénéant [1] constata que l'intensité des raies faibles de l'acide de fréquence 600, 880, 1715 et 1760 K augmenté à mesure qu'on dilue l'acide avec de l'eau. Ces raies ont des fréquences voisines aux fréquences des raies d'intensité moyenne 617, 900 et 1670 K. Fénéant suppose que ces trois raies d'intensité moyenne correspondent aux dimères I et celles d'intensité faible aux dimères II. Elle admet que dans l'acide acétique liquide pur la plupart des molécules donne des dimères en forme de noyau. Quand la concentration de l'acide décroît, les dimères I se transforment d'abord en dimères II, et dans les solutions plus diluées les molécules monomériques s'isolent. Celles-ci sont capables de former des associés avec les molécules d'eau.

**Appareillage.** Le mode de préparation des mélanges déshydratés, l'appareillage, ainsi que la méthode de la pose et de mesures des fréquences des raies ont été décrits dans [2] et [3].

**Résultats.** On a mesuré les fréquences des raies ramanien de l'acide acétique pour l'acide acétique pur et pour les mélanges avec de la pyridine contenant 93.5, 85.4, 78.4, 77.1, 69.6, 62.2, 60.2, 56.7,

51.7, 39.0, 26.8, 19.2 et 8.5% de l'acide par mole. Comme la plupart des raies de l'acide était d'intensité très faible on ne pouvait les décèler que dans les mélanges les plus concentrés.

En examinant les enregistrements photométriques des spectres ramanien des mélanges de différentes concentrations (Fig. 1), on constate que l'intensité de la raie de l'acide de fréquence 1666.3 K est affaiblie et une raie nouvelle de fréquence 1720 K environ apparaît.

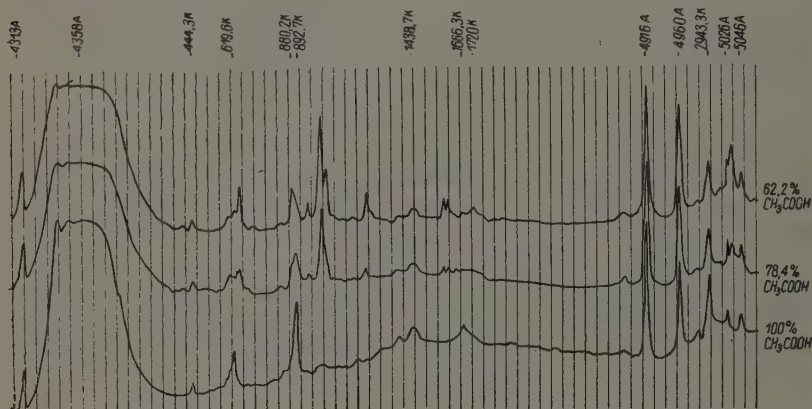


Fig. 1

On observe aussi l'affaiblissement de la raie de l'acide de fréquence 892.7 K et, dans les mélanges contenant moins de 77% d'acide par mole, apparaît une bande dont le maximum correspond à la fréquence 880.2 K. Son existence était déjà signalée dans [2]. Cette bande est formée par les deux raies mentionnées ci-dessus et par la raie de la pyridine de fréquence 888.3 K. Son apparition est tout-de-même liée avec la présence des molécules de l'acide acétique modifiées et non des molécules de la pyridine. Dans les études préliminaires des spectres ramanien du mélange de la pyridine avec l'acide formique on n'a pas trouvé cette bande, qui cependant est visible dans les spectres des mélanges de la pyridine avec les acides acétique et butyrique. Dans les spectres d'oscillation des acides organiques la raie de fréquence 890 K environ correspond aux oscillations de valence de la liaison C—C qui n'existe pas dans l'acide formique. Les raies nouvelles semblent être alors analogues à celles de fréquences 880 et 1715 K trouvées par Fénéant dans les spectres des solutions aqueuses de l'acide acétique.

Les résultats des mesures sont rassemblés dans le Tableau I. Pour la raie nette de fréquence 2943.3 K ils peuvent être considérés comme exacts à 0.5 K près, par rapport aux spectres des mélanges de différentes concentrations. Les autres raies sont diffuses et les résultats des mesures

sont moins précis. On observe des déplacements de la raie nette qui vient d'une manière continue avec la concentration.

**Conclusions.** Dans les spectres ramanien des mélanges étudiés on observe deux raies nouvelles dont les fréquences 880.2 et 1720 K sont proches de celles des deux raies 880 K et 1720 K qui, d'après Fénéant [1], correspondent aux dimères II. On peut donc supposer que dans les mé-

TABLEAU I

% mole  $\text{CH}_3\text{COOH}$ 

100	93.5	85.4	78.4	77.1	69.6	62.2	60.2	56.7	51.7	39.0	26.8	19.2	8.5
444.3	+	+	+	+	—	—	—	—	—	—	—	—	—
619.6	619.5	+	+	+	—	—	—	—	—	—	—	—	—
—	—	—	891.7	+	+	880.2	880.1	880.1	879.7	+	+	+	+
892.7	892.7	892.0	891.7	891.8	+	—	—	—	—	—	—	—	—
1435.7	+	+	—	—	—	—	—	—	—	—	—	—	—
1666.3	+	+	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	1720	+	+	+	+	+	—	—	—
2943.3	2942.3	2941.8	2940.7	2940.3	2939.5	2938.9	2938.9	2938.5	2938.5	—	—	—	—

langes d'acide acétique et de pyridine les molécules d'acide subissent des transformations analogues à celles qui ont lieu dans les solutions aqueuses. Les molécules dimériques qui existent dans l'acide acétique pur sous forme de noyau, prennent, à mesure qu'on dilue l'acide avec de la pyridine, d'abord la forme de chaîne et ensuite apparaissent des molécules monomériques.

Les déplacements continus peuvent s'expliquer selon les conclusions du communiqué précédent [3] par l'influence du moment dipolaire des molécules de la pyridine sur celles de l'acide acétique.

Dans [2] on a pris d'une manière erronée les raies de mercure 5026 et 5046 Å pour les raies ramanien de l'acide acétique de fréquence 3049 et 3126 K.

Je tiens à rendre hommage à mon regretté Maître, feu Professeur S. Pińkowski, pour l'aide et l'encouragement qu'il m'a prodigués dans l'élaboration de ce travail.

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## General Properties of Ideal Eutectic Systems. II

by

W. MALESIŃSKI

*Presented by W. ŚWIEȚOSŁAWSKI on March 9, 1955*

In a preceding paper [1] a classification of simple eutectic systems was given with the assumption that for a series of substances closely related structurally and chemically the relations determining the solubility curve may be expressed by the equation:

$$(1) \quad T'_i = f\left(\frac{x_i}{m_i}\right),$$

$T'_i$  stands for the partial freezing temperature of component  $i$  being in equilibrium with the liquid phase containing  $x_i$  mole fraction of that component;  $m_i$  is a constant eutectic parameter of component  $i$ , its value does not depend upon the temperature. For two other deliberately chosen components at the equilibrium temperature we may write:

$$(2) \quad f\left(\frac{x_1}{m_1}\right) = f\left(\frac{x_2}{m_2}\right).$$

Because there is only one value  $x$  for a given component at a given equilibrium temperature, we conclude that

$$(3) \quad \frac{x_1}{m_1} = \frac{x_2}{m_2} \quad \text{or} \quad \frac{x_1}{x_2} = \frac{m_1}{m_2}.$$

Equation (3) expresses the relation existing between the two ideal solubility curves (called often eutectic branches), which may be formulated as follows: the ratio of the concentrations in the liquid phase of two deliberately chosen components in a two- three- or multicomponent eutectic system, being in equilibrium with pure solid phases of these components, remains constant. In other words, the ratio of the solubilities expressed in mole fractions of two components does not depend upon temperature. In Fig. 1 this relation is represented graphically. Consequently, if the values  $m_i/m_j = k_{ij}$  are given, it is possible to draw

all of the curves representing the eutectic branches on the basis of the shape of one of them.

There is another consequence resulting from equation (1), namely, at any temperature, including the eutectic one, relation (3) remains unchanged for any pair of the components of the system. If we take into consideration a binary ideal eutectic system, viz., that at the eutectic point  $x_1 + x_2 = 1$ , we may rewrite equation (3) in the following manner:

$$(4) \quad x_1 = \frac{m_1}{m_1 + m_2} \quad x_2 = \frac{m_2}{m_1 + m_2}.$$

These two relations define the composition of the eutectic mixture, expressing it in terms of  $m_1$  and  $m_2$ . For a  $k$ -component system the mole fraction of component  $i$  may be calculated in the same way

$$(5) \quad x_i = \frac{m_i}{\sum_{i=1}^k m_i},$$

where  $m_i$  is the constant eutectic parameter of component  $i$ .

Another property of the ideal eutectic systems consists in the general form in which the ideal solubility curve of the eutectic mixture may be expressed. Knowing that for a binary eutectic mixture in a system composed of any number of components  $x_1/x_2 = \text{const.}$ , we may write:

$$(6) \quad x_1 + x_2 = x_{E_{12}}.$$

We call  $x_{E_{12}}$  a mole fraction of the eutectic mixture of components 1 and 2. According to one of the conclusions given in a preceding paper [1], we may use for components 1 and 2 the following two relations:

$$(7) \quad x_1 = m_1 f^{-1}(T'_1) \quad x_2 = m_2 f^{-1}(T'_2).$$

The intersection curve of two surfaces (7) expresses the solubility of the eutectic mixture  $E_{12}$ . Then at a given partial freezing temperature of eutectic mixture  $T'_{E_{12}}$ , both general equations (7) must be fulfilled:

$$(8) \quad x_1 = m_1 f^{-1}(T'_{E_{12}}) \quad x_2 = m_2 f^{-1}(T'_{E_{12}}).$$

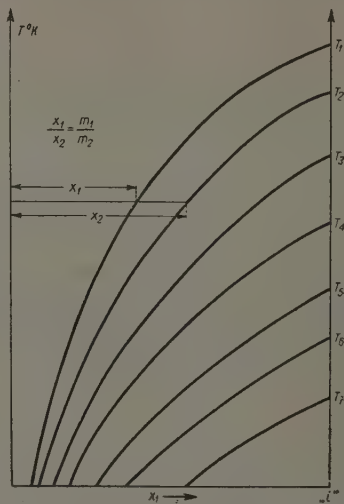


Fig. 1. Ideal solubility curves corresponding to the constant relation:

$$\frac{x_i}{x_j} = \frac{m_i}{m_j} = k_{ij}$$

Combining equations (8) with (6) we obtain:

$$(9) \quad x_{E_{12}} = x_1 + x_2 = (m_1 + m_2) f^{-1}(T'_{E_{12}})$$

or

$$(10) \quad T'_{E_{12}} = f\left(\frac{x_{E_{12}}}{m_1 + m_2}\right).$$

A similar consideration leads us to the conclusion that the partial eutectic freezing temperature for an ideal eutectic mixture composed of  $k$ -components is expressed by the equation:

$$(11) \quad T'_{E_k} = f\left(\frac{x_{E_k}}{\sum_{i=1}^k m_i}\right).$$

Let us consider the ideal solubility of the binary noneutectic mixture  $M_{12}$ , containing an excess of component 1 as compared with the composition of the eutectic mixture  $E_{12}$ . In this case the ratio of the mole fraction  $\frac{x_2}{x_1} = a$  is constant and lower than that which corresponds to the eutectic mixture  $E_{12}$ . For this reason

$$a < \frac{m_2}{m_1}.$$

In the considered case:

$$(12) \quad x_{M_{12}} = x_1 + x_2,$$

where  $x_{M_{12}}$ , denotes the mole fraction of mixture  $M_{12}$  in the solution.

Finally, we have:

$$(13) \quad x_1 = \frac{x_{M_{12}}}{1 + a}.$$

If equilibrium is established between the infinitesimal amount of component 1 and the solution (component 2 is found exclusively in the solution) the partial freezing temperature  $T_1$  is represented by the equation:

$$(14) \quad T'_1 = f\left(\frac{x_1}{m_1}\right).$$

Substituting (13), we obtain:

$$(15) \quad T'_1 = f\left(\frac{x_{M_{12}}}{m_1(1 + a)}\right).$$

Equation (15) represents the temperature at which the solid phase of component 1 disappears when the mixture  $M_{12}$  having a non-eutectic composition is dissolved in the solvent composed of all the components of the system except 1. If  $a = 0$ , then  $x_2 = 0$ ,  $x_{M_{12}} = x_1$  and (15) is reduced to equation (14).

## Summary

Starting with the general equation (1), some of the properties of eutectic systems composed of chemically and structurally related compounds were formulated. In particular, the following relations were given:

a) The solubility ratio of different compounds at the same temperature is constant and equal to the ratio  $m_i : m_j$  of the eutectic parameters.

b) The composition of a  $k$ -component eutectic mixture is determined by the eutectic parameter in the following way:

$$x_i = \frac{m_i}{\sum_{i=1}^k m_i}$$

c) The solubility curves of the pure component and the solubility curve of the mixture of these components, having eutectic or non-eutectic composition, are expressed by the same universal function and by the same eutectic parameters characterizing individually each of the components. The parameters do not depend upon the temperature.

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## Ternary Ideal Eutectic Systems. III

by

W. MALESIŃSKI

*Presented by W. ŚWIĘTOSŁAWSKI on March 9, 1955*

Several years ago Świątosławski [1], basing himself on experimentally established facts, suggested that ternary eutectic systems should be divided into two groups: ideal and non-ideal. In Fig. 1 a graphical presentation of an ideal ternary eutectic system is given. It can be concluded from the graph that the main property of an ideal ternary eutectic system consists in the following phenomena: three lines,  $AE_{BC}$ ,  $BE_{AC}$  and  $CE_{AB}$ , which join points  $A$ ,  $B$  and  $C$  of the concentration triangle with three others representing the composition of the three binary eutectics  $E_{AC}$ ,  $E_{BC}$  and  $E_{AB}$ , cross one another at a common point  $E_{ABC}$ .

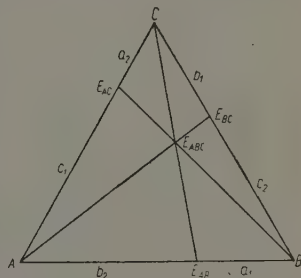


Fig. 1. Ternary ideal eutectic system

This condition is fulfilled when

$$(1) \quad a_1 b_1 c_1 = a_2 b_2 c_2.$$

In Fig. 1 the values  $a_1$ ,  $b_1$ ,  $c_1$ ,  $a_2$ ,  $b_2$  and  $c_2$  are graphically represented. They correspond to the mole fraction of each of the components in binary eutectics. The condition that the ternary eutectic mixture is located in the common crossing point of the three lines is made clear by the following equations:

$$(2) \quad \frac{a}{b} = \frac{a_1}{b_2}; \quad \frac{b}{c} = \frac{b_1}{c_2}; \quad \frac{c}{a} = \frac{c_1}{a_2}.$$

Symbols  $a$ ,  $b$ ,  $c$  represent the mole fraction of the components in the ternary eutectic mixture. The question arises, however, as to whether the condition with regard to the general properties examined in the two previous papers [2] are fulfilled, if the ternary eutectic system

TABLE I

Compo- nent	S y s t e m	P arame- ter B	Composition of binary eutectic mixtures						Composition of ternary eutectic mixtures	
			$E_{AB}$		$E_{BC}$		$E_{BC}$		$x^0/\%$ calc.	$x^0/\%$ exp.
			$x^0/\%$ calc.	$x^0/\%$ exp.	$x^0/\%$ calc.	$x^0/\%$ exp.	$x^0/\%$ calc.	$x^0/\%$ exp.		
1	A	1.000	30.9	31	54.9	55.2	—	—	24.6	23
	B	2.24	69.1	69	—	—	73.1	72.5	55.1	56.5
	C	0.823	—	—	45.1	44.8	26.9	27.5	20.3	20.5
2	A	1.000	72.2	72.5	75.7	75.5	—	—	58.7	57.7
	B	0.384	27.8	27.5	—	—	54.5	54.8	22.5	23.2
	C	0.321	—	—	24.3	24.5	45.5	45.2	18.8	19.1
3	A	1.000	73.6	74.6	82.0	81.4	—	—	63.4	67
	B	0.358	26.4	25.5	—	—	62.0	63	22.7	20
	C	0.219	—	—	18.0	18.6	38.0	37	13.9	13
4	A	1.000	50.4	47	73.5	77	—	—	42.7	38
	B	0.984	49.6	53	—	—	73.2	70	42.0	43
	C	0.360	—	—	26.5	23	26.8	30	15.3	19
5	A	1.000	58.1	57	85.4	86	—	—	52.9	52
	B	0.720	41.9	43	—	—	80.9	80	38.1	39
	C	0.172	—	—	14.6	14	19.1	20	9.0	9
6	A	1.000	56.2	57	36.2	35.5	—	—	28.2	25
	B	0.779	43.8	43	—	—	30.6	31.3	22.0	20
	C	1.760	—	—	63.8	64.5	69.4	68.7	49.8	55
7	A	1.000	42.0	43	29.6	31	—	—	22.1	20.2
	B	1.38	58.0	57	—	—	39.1	40	30.5	31.8
	C	2.15	—	—	70.4	69	60.9	60	47.4	48.0
8	A	1.000	12.4	12.4	31.0	31.0	—	—	9.7	9.5
	B	7.06	87.6	87.6	—	—	76.0	76	68.6	69.5
	C	2.227	—	—	69.0	69.0	24.0	24	21.7	21
9	A	1.000	16.3	15.8	39.1	40	—	—	13.0	12.7
	B	5.14	83.7	84.2	—	—	76.7	76	66.8	68.7
	C	1.560	—	—	60.9	60	23.3	24	20.2	18.6

10	A B C	o-nitrotoluene m- p-	1.000 0.829 0.362	54.7 45.3 —	52 48 —	80.7 — 19.3	76 — 24	— 69.6 30.4	— 67 33	45.7 37.8 16.3	42 44 14
11	A B C	sulphonal naphthol salol	1.000 1.000 1.49 9.49	40.2 59.8 — —	39 61 — —	9.5 — 90.5 —	10 — 90 —	— 13.6 86.4	— 13 87	8.3 12.5 79.2	6 14 80
12	A B C	di (o-nitrophenyl) carbonate di (o-, p'-nitrophenyl) carbonate di (p-nitrophenyl) carbonate	1.000 0.555 0.517	64.3 35.7 —	64.7 35.3 —	65.9 34.1 —	65.8 — 34.2	— 51.8 48.2	— 52.5 47.5	48.3 26.8 24.9	49.5 23.8 26.7
13	A B C	naphthalene benzene m-xylene	1.000 7.62 23.000	11.6 88.4 —	13.4 86.6 —	4.2 — 95.8	3.7 — 96.3	— 21.1 78.8	— 27.6 72.4	3.2 24.1 72.5	2.3 27.3 70.4
14	A B C	naphthalene benzene toluene	1.000 5.80 51.5	14.7 85.3 —	13.4 86.6 —	1.9 — 98.1	2.18 — 97.82	— 10.1 89.9	— 9.07 90.93	1.7 9.9 88.4	1.42 12.75 85.76
15	A B C	naphthalene m-xylene toluene	1.000 20.6 69.9	4.6 95.4 —	3.7 96.3 —	1.4 — 98.6	2.18 — 97.82	— 22.9 77.1	— 18 82.0	1.1 22.7 76.2	2.0 19.0 79.0
16	A B C	p-xylene o- m-xylene	1.000 3.15 6.52	24.1 75.9 —	24.3 75.7 —	13.3 — 86.7	13.3 — 86.7	— 32.6 67.4	— 32.8 67.2	9.4 29.5 61.1	9.5 28.1 62.4
17	A B C	p-xylene o- ethylbenzene	1.000 3.15 38.43	24.3 75.7 —	24.3 75.7 —	2.5 — 97.5	2.5 — 97.5	— 7.6 92.4	— 7.7 92.3	2.4 7.4 90.2	2.3 7.5 90.2
18	A B C	p-xylene m- ethylbenzene	1.000 6.92 37.0	12.6 87.4 —	13.3 86.7 —	2.6 — 97.4	2.5 — 97.5	— 15.8 84.2	— 16.5 83.5	2.2 15.4 82.4	2.2 17.8 80.0
19	A B C	benzene m-xylene toluene	1.000 2.48 10.65	28.7 71.3 —	27 73 —	8.6 — 91.4	9.07 — 90.93	— 18.9 81.1	— 18.0 82.0	7.1 17.6 75.3	14.2 16.5 69.3
20	A B C	o-xylene m- ethylbenzene	1.000 2.16 11.45	31.7 68.3 —	32.8 67.2 —	8.0 — 92.0	7.7 — 92.3	— 15.8 84.2	— 16.5 83.5	6.8 14.8 78.4	7.0 15.5 77.5

is an ideal one according to Świątosławski's definition. For proving this, let us use the symbols  $m_1, m_2, m_3$  for designating the constant eutectic parameters of the three components  $A, B, C$ . According to previous considerations [2], we may write the following equations:

$$(3) \quad \begin{aligned} a_1 &= \frac{m_1}{m_1 + m_2}; & a_2 &= \frac{m_1}{m_1 + m_3}; \\ b_1 &= \frac{m_2}{m_2 + m_3}; & b_2 &= \frac{m_2}{m_1 + m_2}; \\ c_1 &= \frac{m_3}{m_1 + m_2}; & c_2 &= \frac{m_3}{m_2 + m_3}; \end{aligned}$$

which fulfill the condition that  $a_1 b_1 c_1 = a_2 b_2 c_2$ .

On the other hand, we may express the composition of the ternary eutectic mixture in terms of values  $m_1, m_2, m_3$  as follows:

$$(4) \quad a = \frac{m_1}{m_1 + m_2 + m_3}; \quad b = \frac{m_2}{m_1 + m_2 + m_3}; \quad c = \frac{m_3}{m_1 + m_2 + m_3};$$

because:

$$(5) \quad x_i = \frac{m_i}{\sum_{i=1}^k m_i}.$$

Then the number of components  $k$  is equal to 3.

It is easy to see that the conditions of equations (2) are fulfilled if the relations (3) and (4) are correct. In the same way it is possible to prove that Świątosławski's other scheme [3] given for quaternary and polycrystalline systems is also correct. For instance, for an ideal eutectic system composed of five components  $A, B, C, D, F$  it is possible to consider that it is composed of component  $A$  and two binary eutectics  $E_{BC}$  and  $E_{DF}$ , or even of two components  $A$  and  $B$  and one ternary eutectic.

In both cases Gibbs's concentration triangle may be used for graphical presentation of the phenomena taking place in those systems.

Because a relatively large number of ternary eutectic mixtures formed by chemically and structurally closely related substances have been examined [4] it is possible to determine whether or not these systems belong to ideal or almost ideal ones. The results are shown in Table I. The parameters  $m_i$  of the components have been calculated from the experimental composi-

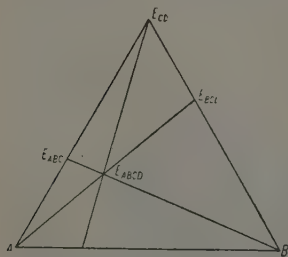


Fig. 2. Scheme representing on the Gibbs triangle of concentrations a quaternary ideal eutectic system

tions of binary eutectic mixtures. In Table I the following data are given: a) the mean values of the parameters  $m$ , taking one of the components as reference compound ( $m=1$ ), b) the compositions of the binary and ternary eutectics calculated from equations (3) and (4) in comparison with experimental ones.

It should be noted that in the case of five out of 20 systems (3, 4, 6, 10, 19) no satisfactory agreement was found. The differences between the calculated and the observed composition of ternary eutectics are less than 1% mole fraction for six systems (2, 5, 8, 14, 17, 20) and between one and three per cent for the nine remaining systems. The conclusion may be made that in this way the composition of ternary eutectic mixtures may be calculated with a satisfactory agreement. This is an indication that a large number of ternary eutectics formed by chemically or structurally related organic substances often form ideal or almost ideal systems.

#### Summary

1. The conditions expressed by equations (1) and (2) were given for defining the ideal eutectic systems described by Świątosławski.

2. It was shown that the general properties of ideal three- and polycomponent eutectics, examined in the two preceding papers [2] are in close agreement with those defined by Świątosławski.

3. A table is given showing that the composition of ternary eutectics formed by substances closely related both chemically and structurally may be calculated with a satisfactory agreement.

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# The Change of the Mutual Exchange Ability of the Same Pair of Anions or Cations in Dependence on the Size of the Accompanying Ions. I

by

T. PENKALA

*Presented by W. ŚWIĘTOSŁAWSKI on March 22, 1955*

In a paper published in *Roczniki Chemii*, W. Świątosławski [1], [2] has given a scheme of gradual transition of organic compounds in binary mixtures from solid solutions with unlimited mutual solubility to ideal eutectics. This transition is correlated with the gradual increase of the difference in shape and size of the molecules of the substances in the binary systems. On the basis of an adequate comparison of experimental data collected from literature, it has been observed that the given scheme is also true for binary systems of inorganic compounds if we examine the increasingly difficult mutual exchange ability of the same pair of anions or cations in relation to the influence of the size of the accompanying ions. With the decrease of mutual exchange ability of the same pair of ions in the crystalline network we pass, conforming to W. Świątosławski's scheme, from solid solutions with unlimited mutual solubility to solid solutions with limited solubility, and finally to ideal eutectics with pure solid phases of the two components.

As Goldschmidt [3] and other authors [4] have shown for binary systems, mutual exchange ability appears in ions, the radii of which do not differ from each other by more than 15%. Goldschmidt has observed that the mutual exchange ability of the same pair of ions depends on the type of the space network and has demonstrated that in complicated structures of multiatom compounds there could appear significant structural gaps, which caused an increase of the mutual ion exchange ability. In binary systems of inorganic compounds characterized by a simple chemical composition and a simple structural type the influence of the size of cations on mutual exchange ability of the same pair of anions can be observed, as shown by the following examples.

Comparing three binary systems KOH-KF, NaOH-NaF and LiOH-LiF (Fig. 1), we can state that the mutual exchange of the same pair of anions occurs the easier, the greater are the cations bound with the anions. The radii of the ions in these systems and in the systems mentioned below are the following:  $F^-$  — 1.33 Å,  $OH^-$  — 1.53 Å,  $Cl^-$  — 1.80 Å,  $Br^-$  — 1.96 Å,  $I^-$  — 2.20 Å,  $Li^+$  — 0.78 Å,  $Na^+$  — 0.98 Å,  $K^+$  — 1.33 Å,  $Ba^{++}$  — 1.43 Å,  $Sr^{++}$  — 1.27 Å.

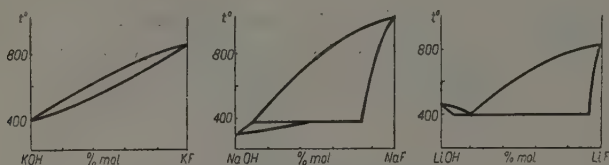


Fig. 1. Increase of mutual exchange ability of  $F^-$  and  $OH^-$  with the increase in size of cations

We also see the same relationship in the systems: 1) KOH-KCl, which forms a solid solution with a small miscibility gap; 2) NaOH-NaCl, which forms a solid solution with a significant greater miscibility gap; 3) LiOH-LiCl, which forms a eutectic ( $LiOH + 3LiCl \cdot 2LiOH$ ). This re-

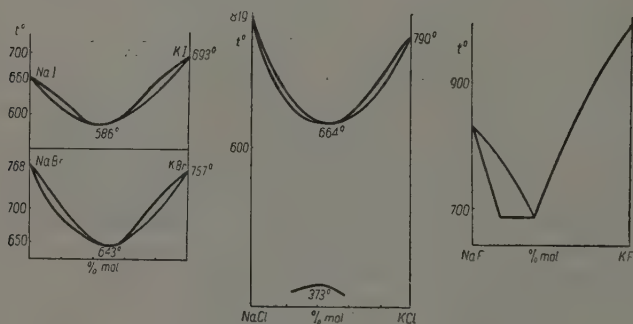


Fig. 2. The gradual decrease of the minimum point of the solidus curve is related with the miscibility decrease of the components in the solid solutions

gularity occurs also in the systems: KCl-KI, which forms a solid solution, and NaCl-NaI, which forms a eutectic composed from the pure component NaCl and the solid solution  $Na(Cl, I)$ .

Equally, the mutual exchange of the cations is the better the greater the anions. This relation is seen on the following example: (Fig. 2)

NaI-KI and NaBr-KBr form solid solutions, NaCl-KCl form a solid solution which undergoes, in lower temperatures, a partial separation, NaF-KF form a eutectic composed of the pure phase KF and mix-crystals (Na, K)F.

The example given on Fig. 2 evidences the relationship between the decrease of the miscibility of the components in the solid solutions and increase in curvature of the solidus curves in such a way that the minimum of the freezing temperature gradually decreases. The difference between the freezing temperature of the lower freezing component and the minimum point in the following mixtures are: KI-NaI —  $74^{\circ}$ , KBr-NaBr —  $114^{\circ}$ , KCl-NaCl —  $126^{\circ}$ . The increase of the concavity of the solidus curve can be found too in the solid solutions NaBr-LiBr and NaCl-LiCl. In the NaBr-LiBr system the minimum point of the solidus curve lies only  $27^{\circ}$  below freezing point of the lower freezing component. But in the NaCl-LiCl system the smaller anion depresses the mutual exchange ability of the same pair of cations: this appears in the fact that the minimum point lies  $62^{\circ}$  C. below the freezing temperature of the lower freezing component, and, besides, in lower temperatures the solution shows the demixing of the components.

A similar relationship, viz., the lowering of the minimum of the solidus curve with the decrease of miscibility of the components, is seen, in the systems formed by analogous salts of two valency metals. For example, the solidus curve of the solid solution (Ba, Sr)F<sub>2</sub> has a deeper minimum than the curve (Ba, Sr)Cl<sub>2</sub>. The freezing points of the pure components are: BaF<sub>2</sub> —  $1280^{\circ}$ , SrF<sub>2</sub> —  $1260^{\circ}$ , BaCl<sub>2</sub> —  $955^{\circ}$ , SrCl<sub>2</sub> —  $870^{\circ}$ . In the (Ba, Sr)F<sub>2</sub> system the minimum point —  $1080^{\circ}$  lies  $180^{\circ}$  C. below the freezing point of the lower freezing component. In the (Ba, Sr)Cl<sub>2</sub> system the temperature at the minimum point —  $847^{\circ}$  — is only  $23^{\circ}$  C. below the melting point of SrCl<sub>2</sub>. The observed regularity concerns binary systems of inorganic compounds which do not show too strong ionic polarization.

#### Summary

1. It has been observed on crystals of halide salts, which do not show too strong ionic polarization, that the greater the haloide ions, the easier the mutual cation exchange, and the greater the cations the easier the mutual exchange of the same pair of anions.

2. It has been found that W. Świątosławski's scheme concerning a gradual transition from solid solutions to ideal eutectics, is also true for binary systems of inorganic compounds in the case when mutual exchange of the same pair of ions becomes more and more difficult.

3. With the decrease of miscibility of the components in solid solutions the tendency to a gradual decrease of the minimum point of the "solidus" curve has been observed.

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# The Gradual Transition from Solid Solutions to Eutectics in Binary Systems of Inorganic Compounds. II

by

T. PENKALA

*Presented by W. ŚWIĘTOSŁAWSKI on March 22, 1955*

In the preceding paper [1] it has been demonstrated that the scheme given by W. Świątosławski concerning the gradual transition from solid solutions without miscibility gap through solid solutions with miscibility gap to ideal eutectics (Fig. 1), is true in the case of gradual increase of the difference in structure and size of the molecules in the organic substances which form binary systems.

In this paper the literature data concerning binary systems of monovalent metal chlorides has been collected and a gradual transition from solid solutions to ideal eutectics, similar to W. Świątosławski's scheme for organic compounds, has been observed.

In organic compound systems the formation of a solid solution or a eutectic depends, according to the investigations of Goldschmidt [4], [5], on the crystal-chemical resemblance of the ions; this resemblance is correlated with the ionic radius size and the polarization tendency of the ions. In halide salts of monovalent metals the weakest polarization is shown by fluorides and chlorides, since the polarization of the anions increases with their dimensions. In these systems the decisive factor which influenced the formation of solid solutions is the size of mutual exchanging ions, in the same way as the size of molecules in molecular networks of organic compounds. Hence the relationship given by W. Świątosławski for organic compound systems is also true in case of binary systems of ionic compounds with a not too strong ionic polarization. In the examined series of binary

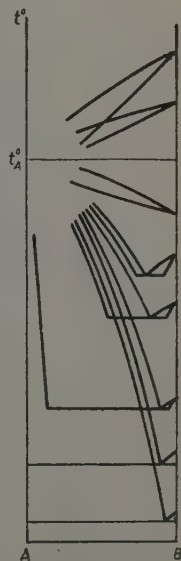


Fig. 1. W. Świątosławski's scheme of gradual transition from solid solutions to eutectics in organic compound systems

systems, shown on Fig. 2, a gradual transition from solid solutions without a miscibility gap to eutectics through solid solutions with a minimum, can be observed. These solutions show in the lower tem

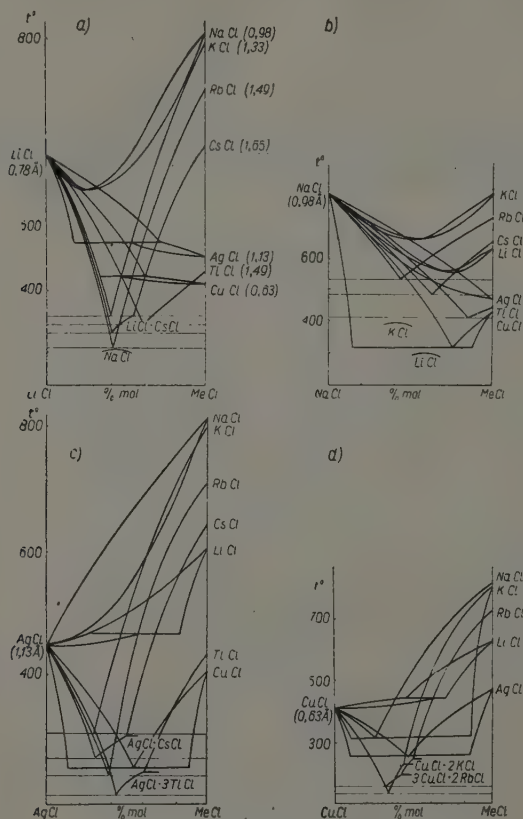


Fig. 2. Mutual exchange ability of monovalent cations in crystalline networks of metal chlorides. In parenthesis the cation radii, in Å

perature range a spontaneous demixing of the components (Fig. 2b) or a gradual extension of the miscibility gap when the difference in size of the cations increases (Fig. 2, c, d).

The relationship discussed, regarding the gradual transition from eutectics to solid solutions is also true in case of mutual exchange of anions (Fig. 3).

In the systems discussed it can be observed that in case of a common anion and a great difference in size of the cations double salts are

formed and the eutectics are composed of double salts and of the main component (Fig. 2a,c,d). In the case of a large difference in size of the anions in binary systems of salts with a common cation a similar influence has been noticed. For example, the NaOH-NaCl system forms a solid solution, NaOH-NaBr, an ideal eutectic of the components, but in the NaOH-NaI system a eutectic  $\text{NaOH} + 3\text{NaI} \cdot 2\text{NaOH}$  is formed.

It has been noticed that there is a reduction of miscibility of the components in the solid solutions when the tendency to depress the solidus curve minimum increases. With the increase of the difference in

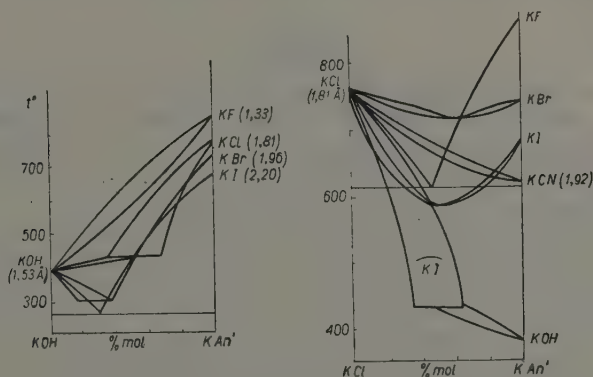


Fig. 3. Gradual transition from solid solutions to eutectics in the case of mutual exchange of anions. In parenthesis: the anion radii figures

size of the anions in the solid solutions  $\text{K}(\text{Cl}, \text{CN})$ ,  $\text{K}(\text{Cl}, \text{Br})$ ,  $\text{K}(\text{Cl}, \text{I})$  shown in Fig. 3, the solidus curve minimum gradually decreases. Similarly the solid solution  $(\text{Na}, \text{Ag})\text{Cl}$  shows no minimum, but with greater difference in cation size, the miscibility in the  $(\text{Na}, \text{K})\text{Cl}$  and  $(\text{Na}, \text{Li})\text{Cl}$  solutions is lower, which is seen in the demixing into components of solid solutions at lower temperatures and the disappearance of a minimum on the solidus curve (Fig. 2b).

In the case of gradual transition from solid solutions without miscibility gap to eutectics, caused by increased difference in ion size, there can be distinguished the following intermediate stages:

- 1) solid solutions without a minimum;
- 2) solid solutions with a minimum, which in lower temperatures do not undergo demixing into components and have the tendency to an increasing depression of the minimum point with the increase of the difference in dimensions of the exchanging ions;
- 3) solid solutions which separate into components at lower temperatures;

- 4) solid solutions with a minimum, which show a separation into components at temperatures near to that minimum;
- 5) solid solutions which demix into components at temperatures equal to the minimum temperatures;
- 6) solid solutions with a small miscibility gap, the formation of which is associated with a more distinctly pronounced miscibility gap so that its peak is found in the liquid phase area;
- 7) solid solutions with a large miscibility gap;
- 8) ideal eutectics of the components;
- 9) eutectics formed by a double salt and one of the components.

#### Summary

1. It has been observed that the scheme given by W. Świątosławski concerning the gradual transition of binary mixtures of organic compounds from solid solutions through solid solutions with limited mutual solubility to ideal eutectics may also be applied to inorganic ionic compounds without or with a weak ionic polarization.

2. A gradual increase in curvature of the solidus curve in case of the solid solutions with a minimum and a gradual transition through solid solutions with mutual solubility to eutectics of solid solutions has been pointed out.

3. In binary mixtures of metal chlorides with common anion and great difference in size of the cation, the formation of a eutectic double salt and of the main components is clearly pronounced. A similar influence in case of a large difference in size of the anions in binary mixtures of salts with common cation is evident.

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## The Influence of Ionic Polarization on the Formation of Solid Solutions and Eutectics. III

by

T. PENKALA

*Presented by W. ŚWIĘTOSŁAWSKI on March 22, 1955*

The negative influence of ionic polarization on the formation of solid solutions confirmed by Goldschmidt [1], [2] can be investigated on the basis of the scheme given by W. Świątosławski [3], [4] concerning the gradual transition from solid solutions to eutectics and organic mixtures. This scheme is also valid for binary systems of inorganic compounds with not too strong ionic polarization. Deviations from this scheme indicate the influence exerted by ionic polarization.

In Fig. 1 binary systems composed by AgI and iodides of other metals of the first group in the periodical system have been shown. According to Goldschmidt [2] the Ag ion caused a very strong polarization activity on the large iodine anion so that the distance between the centres Ag and I ions is smaller than the sum of the radii of these ions. Hence at the formation of solid solutions by AgI and other iodides, the Ag ion behaves as if its radius were smaller.

The Ag ion substitutes the much smaller Li and Cu ions in solid solutions of (Ag, Li)I and (Ag, Cu)I, but do not substitute the Na ion in the AgI-NaI system, although the Na ion is similar in size. A similar relationship can be observed in binary systems formed by NaI-KI and NaI-AgI. There exists a solid solution of (Na, K)I although the difference in size of the cations is considerable, but the NaI-AgI system forms a eutectic, although the difference in size of the cations here is rather smaller.

In binary systems of bromides of monovalent metals, we can find some deviations, which confirm the negative ionic polarization influence on the miscibility of components with similar ionic dimensions. And so there exists a solid solution of (K, Na)Br, but KBr and AgBr form a eutectic, although the difference in size of the cations is here smaller.

In case of binary systems without ionic polarization the mutual exchange of the same pair of cations takes place more easily if the halide

ions are larger. For example, there exist solid solutions of (K, Na)I and (K, Na)Br, while the solid solution of (K, Na)Cl, in lower temperatures undergo, demixing into pure components, and the KF-NaF mixture

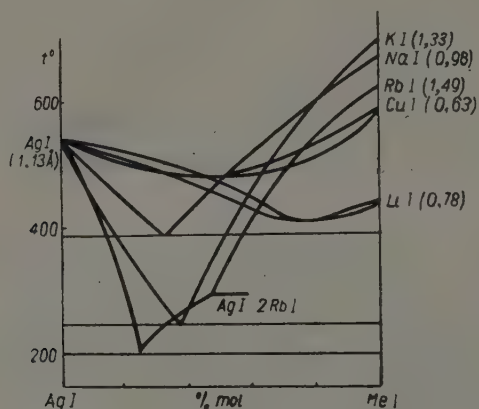


Fig. 1. Binary systems of AgI and iodides of monovalent metals. In parentheses, the radii of the cations in these systems, in Å

forms a eutectic  $\text{KF} + (\text{Na}, \text{K})\text{F}$ . In binary systems of halide salts, in which one of the cations caused a strong polarization, this relationship does not take place. For example: the NaI-AgI system forms a eutectic, while the same pair of cations bound with smaller ions forms solid solutions of (Na, Ag)Br and (Na, Ag)Cl.

### Summary

Deviations from the scheme of gradual transition from solid solutions to ideal eutectics in the case of binary systems of ionic crystals with strong ionic polarization has been observed. These deviations show a certain regularity, viz., the cation with a strong polarization behaves in binary systems as if its size were much smaller than indicated by the figures in the tables of experimentally determined size of ionic radius

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1955: Vol 3 Iss 6

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VOLUME III  
NUMÉRO 6

VARSOVIE 1955

PRINTED IN POLAND

PAŃSTWOWE WYDAWNICTWO NAUKOWE – DZIAŁ CZASOPISM  
WARSZAWA, KRAKOWSKIE PRZEDMIEŚCIE 79

<i>Nakład 1052 + 103 egz.</i>	<i>Rękopis dostarczono 21. V. 1955</i>
<i>Ark. wyd. 4, ark. druk. 3<math>\frac{3}{4}</math></i>	<i>Podpisano do druku 29. VII. 1955</i>
<i>Papier bezdrzewny sat. 80 g kl. III</i>	<i>Druk ukończono w sierpniu 1955</i>
<i>Format B5, 70×100 cm</i>	<i>Zam. prod. 209/53    Cena zł 5.–</i>

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# Involutions of Compact Spaces and a Generalization of Borsuk's Theorem on Antipodes

by

J. W. JAWOROWSKI

*Presented by K. BORSUK on May 2, 1955*

1. In 1932 K. Borsuk proved three theorems about the  $n$ -dimensional sphere  $S_n$ , the most important of which is known under the name "Antipodensatz" (see [1], p. 178). These theorems are closely related to one another. The purpose of this paper is to give a generalization of them. The proof of our theorems will be based on the theorem which is announced by the author in [2].

2. Let  $M$  be a compact metric space. As in [2] we shall consider chains and cycles modulo 2 in  $M$  in the sense of Vietoris.

Let us suppose that the space  $M$  is  $p$ -acyclic modulo 2 and  $\varphi$  is a continuous involution \*) of  $M$ . Then we can construct in  $M$  a sequence of true chains of  $M$

$$\Gamma^p = (\gamma^{-1}, \kappa^0, \gamma^0, \dots, \kappa^p, \gamma^p)$$

called a  $(p, \varphi)$ -system in  $M$ , which is defined as follows:

1°  $\gamma^{-1}$  is the number 1 considered as a  $(-1)$ -dimensional true cycle of  $M$ .

2° For some  $r$  ( $-1 \leq r < p$ ) let an  $r$ -dimensional true cycle  $\gamma^r$  of  $M$  be already defined such that  $\varphi(\gamma^r) = \gamma^r$ . Since  $r < p$ , the true cycle  $\gamma^r$  is homologous to zero in  $M$ . Let  $\kappa^{r+1}$  be a true chain in  $M$  such that

$$\kappa^{r+1} = \gamma^r.$$

Then we put

$$\gamma^{r+1} = \kappa^{r+1} + \varphi(\kappa^{r+1}).$$

Thus  $\gamma^{r+1}$  is an  $(r+1)$ -dimensional true cycle in  $M$  and  $\varphi(\gamma^{r+1}) = \gamma^{r+1}$ .

Let  $S_n$  be the unit sphere in the  $(n+1)$ -dimensional Euclidean space  $E_{n+1}$ , i.e. the set of points  $p \in E_{n+1}$  which satisfy the condition  $|p| = 1$ .

\*) i.e. a mapping of  $M$  into itself, which satisfies the condition  $\varphi(\varphi(x)) = x$  for every  $x \in M$ .

Let  $\alpha$  be the antipodal map of  $S_n$ , i. e.  $\alpha(p) = -p$ . Then  $\alpha$  is a continuous involution of  $S_n$ . If  $M$  is a closed  $p$ -acyclic subset of  $S_n$  and  $\alpha(M) = M$ , then the  $(p, \alpha)$ -system in  $M$  is the true antipodal  $p$ -system in  $M$  in the sense of [2]. The theorem, which is announced in [2], for  $p = n$  and  $A = S_n$ , can be formulated as follows:

(A) Let  $\Gamma^n = (\gamma^{-1}, \gamma^0, \gamma^0, \dots, \gamma^n, \gamma^n)$  be an  $(n, \alpha)$ -system in  $S_n$ . Then the true cycle  $\gamma^n$  is not homologous to zero in  $S_n$ .

3. The main result of this paper is the following:

THEOREM 1. Let  $M$  be an  $n$ -acyclic modulo 2 compact metric space and let  $\varphi$  be a continuous involution of  $M$ . Then every continuous mapping  $f$  of  $M$  into  $S_n$  which satisfies the condition  $f(\varphi(x)) \neq f(x)$ , for every  $x \in M$ , maps the  $k$ -dimensional homology groups  $B^k(M)$  modulo 2 of  $M$  onto the  $k$ -dimensional homology groups  $B^k(S_n)$  modulo 2 of  $S_n$ , for every  $k = -1, 0, 1, 2, \dots$

Proof. Since the homology groups  $B^k(S_n)$  of  $S_n$  are zero for every  $k \neq n$ , and the  $n$ -dimensional homology group  $B^n(S_n)$  contains only two elements, it remains to prove, that  $f$  maps some  $n$ -dimensional true cycle of  $M$  onto a true cycle of  $S_n$ , which is not homologous to zero in  $S_n$ .

Let  $\Delta^n = (\delta^{-1}, \lambda^0, \delta^0, \dots, \lambda^n, \delta^n)$  be a  $(n, \varphi)$ -system in  $M$ . Let us put

$$g(x) = \frac{f(x) - f(\varphi(x))}{|f(x) - f(\varphi(x))|}^*)$$

for every  $x \in M$ . Since  $f(x) \neq f(\varphi(x))$ ,  $g$  is a continuous mapping of  $M$  into  $S_n$  and satisfies the condition

$$g(\varphi(x)) = -g(x)$$

for every  $x \in M$ . Hence  $g$  maps the  $(n, \varphi)$ -system  $\Delta^n$  onto the  $(n, \alpha)$ -system  $g(\Delta^n) = (g(\delta^{-1}), g(\lambda^0), g(\delta^0), \dots, g(\lambda^n), g(\delta^n))$  on  $S_n$ . From theorem (A) we conclude that the cycle  $g(\delta^n)$  is not homologous to zero in  $S_n$ .

Furthermore, we observe that, for every  $x \in M$ , the points  $f(x)$  and  $g(x)$  are not antipodal. Indeed, if we suppose that  $f(x) = -g(x)$ , i. e.

$$f(x) = -\frac{f(x) - f(\varphi(x))}{|f(x) - f(\varphi(x))|},$$

then we obtain:

$$(1) \quad f(\varphi(x)) = f(x) \cdot (1 + |f(x) - f(\varphi(x))|).$$

Since  $|f(x)| = |f(\varphi(x))| = 1$ , we conclude from (1) that  $|1 + |f(x) - f(\varphi(x))|| = 1 + |f(x) - f(\varphi(x))| = 1$ , which is impossible, since  $|f(x) - f(\varphi(x))| > 0$ .

The fact that, for every  $x \in M$ , the points  $f(x)$  and  $g(x)$  are not anti-

\*) in the sense of operations with points in the space  $E_{n+1}$ .

podal, proves that the mappings  $f$  and  $g$  are homotopic (see, e.g. [7]). Hence the true cycles  $f(\delta^n)$  and  $g(\delta^n)$  are homologous in  $S_n$ . Since the true cycle  $g(\delta^n)$  is not homologous to zero in  $S_n$ , we conclude that  $f(\delta^n)$  is not homologous to zero in  $S_n$  either.

Therefore, the mapping  $f$  maps the  $n$ -dimensional true cycle  $\delta^n$  of  $M$  onto the  $n$ -dimensional true cycle  $f(\delta^n)$  of  $S_n$ , which is not homologous to zero in  $S_n$ . Thus Theorem 1 is proved.

Since the group  $B^n(S_n)$  is not trivial and since every continuous mapping  $f$  of  $M$  into  $S_n$  homotopic to a constant maps every true cycle  $\gamma^k$  lying in  $M$  onto a true cycle  $f(\gamma^k)$  homologous to zero in  $S_n$ , we deduce from Theorem 1 the following

**COROLLARY 1.** *Let  $M$ ,  $q$  and  $f$  be as in Theorem 1. Then  $f$  is not homotopic to a constant.*

As a simple consequence of Corollary 1, we obtain the following:

**THEOREM 2.** *Let  $M$  and  $q$  be as in Theorem 1. Then, for every continuous mapping  $f$  of  $M$  into the Euclidean space  $E_n$ , there exists a point  $x_0 \in M$ , such that  $f(q(x_0)) = f(x_0)$ .*

For, the mapping  $f$  of  $M$  into  $E_n$  may be considered as a mapping of  $M$  into a proper subset of  $S_n$ , and hence  $f$  is homotopic to a constant. Then, if we suppose that  $f(q(x)) = f(x)$  for every  $x \in M$ , we obtain a contradiction with Theorem 1, which proves Theorem 2.

From Theorem 2 and a lemma of Borsuk (see [1], p. 188) results:

**THEOREM 3.** *Let  $M$  and  $q$  be as in Theorem 2 and let  $M = M_0 + M_1 + \dots + M_n$  be a decomposition of  $M$  into a sum of  $n+1$  closed subsets of  $M$ . Then at least one of the sets  $M_i$  contains an involution pair  $\{x, q(x)\}$ .*

If  $M = S_n$  and  $q$  is the antipodal map, Theorems 1, 2, and 3 reduce to Theorems I, II, and III of [1], respectively. Theorem III of [1], called the Theorem of Borsuk-Lusternik-Schnirelmann, was found and proved first by L. Lusternik and L. Schnirelmann [8] and later by Borsuk [1]. Concerning other analogous theorems see [3], [4], and [5].

If  $M = S_n$  and  $q$  is a continuous involution of  $S_n$ , we obtain Theorems I, II, and III of [1] generalized on the case in which the antipodal map of  $S_n$  is replaced by an arbitrary continuous involution. In particular, Theorem 1 yields

**COROLLARY 2.** *Let  $q$  be a continuous involution of  $S_n$  and let  $f$  be a continuous mapping of  $S_n$  into itself such that  $f(q(x)) \neq f(x)$  for every  $x \in S_n$ . Then the degree of  $f$  is odd.*

This theorem was proved recently by M. A. Krasnosyelsky in another way (see [6]).

**4. THEOREM 4.** *Let  $M$  be an acyclic modulo 2<sup>\*</sup>), compact metric space. Then any continuous involution  $q$  of  $M$  has a fixed point.*

<sup>\*</sup>) The space  $M$  is said to be acyclic modulo 2 if it is  $p$ -acyclic modulo 2 for every  $p$ .

Proof. We can admit (by the known theorem of Urysohn [9]) that  $M$  is a subset of the Hilbert cube  $Q_\omega$ . Let us suppose that  $\varphi(x) \neq x$  for every  $x \in M$ . Since  $M$  is compact, there exists a number  $\varepsilon > 0$  such that  $\varrho(x, \varphi(x)) \geq 2\varepsilon$  for every  $x \in M$ . Let  $r_n$  be the projection of  $Q_\omega$  onto the Euclidean  $n$ -dimensional cube  $Q_n$ , defined for every  $z = (z_1, z_2, \dots) \in Q_\omega$  by the formula

$$r_n(z_1, z_2, \dots) = (z_1, z_2, \dots, z_n, 0, 0, \dots).$$

Then, for every  $\eta > 0$  there exists a number  $n$  such that  $\varrho(z, r_n(z)) < \eta$  for every  $z \in Q_\omega$ . Let  $n$  be such that

$$\varrho(z, r_n(z)) < \varepsilon.$$

Thus  $f = r_n \varphi$  is a continuous mapping of  $M$  into the Euclidean cube  $Q_n$  and

$$\begin{aligned} \varrho(f(x), f(\varphi(x))) &= \varrho(r_n(\varphi(x)), r_n(x)) \geq \varrho(\varphi(x), x) - \varrho(\varphi(x), r_n(\varphi(x))) - \\ &\quad - \varrho(x, r_n(x)) > 2\varepsilon - \varepsilon - \varepsilon = 0. \end{aligned}$$

Hence  $f(\varphi(x)) \neq x$  for every  $x \in M$ . But  $M$  is acyclic and therefore also  $n$ -acyclic and this contradicts Theorem 2. Thus Theorem 4 is proved.

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# Families of Acyclic Compacta in Euclidean $n$ -Space

by

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*Presented by K. BORSUK on April 25, 1955*

1. We shall prove in this note some generalizations of the known theorems on sweeping and some new theorems on the same subject [1]; all this will be done in an unified treatment in which the Vietoris mapping theorem is the principal instrument.

**2. Terminology and notations.** We shall use the Vietoris homology theory. The letter  $m$  will always denote 0 or a natural number  $\geq 2$ . The group of integers reduced mod  $m$  will be denoted by  $\mathfrak{G}_m$ . The homomorphism induced on the  $r$ -th homology group  $H^r(X, \mathfrak{G}_m)$  of the space  $X$  by the mapping  $f: X \rightarrow Y$  will be denoted by  $h'_{f,m}$ . A homomorphism  $h$  will be called *trivial* if the image of the whole group under  $h$  is a single element. A set  $X$  will be called *acyclic mod  $m$  in the dimension  $r$*  if  $H^r(X, \mathfrak{G}_m)$  is trivial. If  $X$  is acyclic mod  $m$  in all dimensions it will be said simply to be *acyclic mod  $m$* . The following theorem is of importance to us:

THE VIETORIS MAPPING THEOREM ([2] or [3]). *Let  $f: X \rightarrow Y$  be a continuous mapping of a compact space  $X$  onto a space  $Y$ . If  $f^{-1}(y)$  is acyclic mod  $m$  for every  $y \in Y$ , then  $h'_{f,m}$  is an isomorphism and is onto.*

Let  $X$  be a compact metric space and let  $\Phi: X \rightarrow 2^Y$  be an upper semi-continuous \*) mapping of  $X$  in the space  $2^Y$  of all non-empty compact subsets of a (metric separable) space  $Y$ . The triple  $\mathcal{F} = \{X, Y, \Phi\}$  will be called a *family*. The set  $X$  will be said to be the *basis* of  $\mathcal{F}$ , the sets  $\Phi(x)$  — the *elements* of  $\mathcal{F}$ , the set  $\bigcup_{x \in X} \Phi(x) \subset Y$  — the *field* of  $\mathcal{F}$ . The field will also be denoted by  $\Phi(X)$ . The family  $\mathcal{F}$  will be said to be *simple* if its elements are disjoint; it will be said to be *acyclic mod  $m$*  if all its elements are acyclic mod  $m$ .

The subset  $F = \bigcup_{x,y} [y \in \Phi(x)]$  of the Cartesian product  $X \times Y$  will be said to be the *graph* of  $\mathcal{F} = \{X, Y, \Phi\}$ . The mapping  $(x, y) \rightarrow x$  (resp.  $(x, y) \rightarrow y$ ) of  $F$  in  $X$  (resp. in  $Y$ ) will be called the *projection*.

\*) For the definition of upper semi-continuous mapping see for instance [4], p. 32.

It is easily seen that the graph and the field of a family are compact sets.

Let  $\mathcal{F}_i = \{X, Y, \Phi_i\}$ ,  $i=1,2$ , be two families. We shall call the family  $\mathcal{F}_1$  a *prolongation* of the family  $\mathcal{F}_2$  if  $\Phi_1(x) \supset \Phi_2(x)$  for every  $x \in X$ . The class of all families acyclic mod  $m$  which are prolongations of a given family  $\mathcal{F}$  will be denoted by  $\mathfrak{P}_m(\mathcal{F})$ .

Let  $\mathcal{F} = \{X, E_n, \Phi\}$  be a family with the field in the Euclidean  $n$ -space  $E_n$ . The subclass of all prolongations of  $\mathcal{F}$  consisting of all those families whose field contains all bounded components of  $E_n - \Phi(X)$  will be denoted by  $\mathfrak{S}(\mathcal{F})$ . In the investigation of  $\mathfrak{S}(\mathcal{F})$  the following lemma will be useful:

LEMMA. Let  $\mathcal{F}_i = \{X, E_n, \Phi_i\}$ ,  $i=1,2$ , be two families and suppose that  $\mathcal{F}_1$  is a prolongation of  $\mathcal{F}_2$ . Let  $j: \Phi_2(X) \rightarrow \Phi_1(X)$  be the identity mapping. If the homomorphism  $h_{j,m}^{n-1}$  is trivial for some  $m$  then  $\mathcal{F}_1 \in \mathfrak{S}(\mathcal{F}_2)$ .

Proof. Suppose that  $\mathcal{F}_1 \notin \mathfrak{S}(\mathcal{F}_2)$ . Then there exists a bounded component  $G$  of  $E_n - \Phi_2(X)$  such that  $G - \Phi_1(X) \neq \emptyset$ . Let  $p_1 \in G - \Phi_1(X)$  and let  $p_2$  belong to the unbounded component of  $E_n - \Phi_1(X)$ . For every  $m$ , the pair  $(p_1, p_2)$  may be considered as an algebraic 0-dimensional cycle  $\alpha$  mod  $m$ . Since this cycle is not homologous to 0 in  $E_n - \Phi_2(X)$  there exists in  $\Phi_2(X)$  an  $(n-1)$ -dimensional true convergent cycle  $\gamma$  mod  $m$  linked mod  $m$  with the cycle  $\alpha$  (see [5] p. 185). Thus,  $\gamma$  is not homologous to 0 in  $\Phi_1(X)$  and we infer that for every  $m$  the homomorphism  $h_{j,m}^{n-1}$  is not trivial.

**3. Prolongations of simple families.** If the family  $\mathcal{F} = \{X, Y, \Phi\}$  is simple then its elements constitute an upper semi-continuous decomposition of  $\Phi(X)$  and the space  $X$  may be considered as the space of this decomposition. The natural mapping of  $\Phi(X)$  onto  $X$  will be denoted by  $\Phi^{-1}$ .

THEOREM 1. Let  $\mathcal{F} = \{X, E_n, \Phi\}$  be a simple family. If the homomorphism  $h_{\Phi^{-1},m}^{n-1}$  is trivial then  $\mathfrak{P}_m(\mathcal{F}) \subset \mathfrak{S}(\mathcal{F})$ .

Proof. Let  $\mathcal{F}_1 \in \mathfrak{P}_m(\mathcal{F})$  and let  $F, F_1$  be the graphs of  $\mathcal{F}, \mathcal{F}_1$  respectively. Since  $\mathcal{F}$  is simple, the projection of  $F$  onto  $\Phi(X)$  is a homeomorphism. Denote its inversion by  $p$ , the projection of  $F_1$  onto  $\Phi_1(X)$  by  $p_1$ , the projection of  $F_1$  onto  $X$  by  $q$ , the identity mapping  $F \rightarrow F_1$  by  $i$ , the identity mapping  $\Phi(X) \rightarrow \Phi_1(X)$  by  $j$  and consider the following diagram

$$\begin{array}{ccccc} F & \xrightarrow{\quad} & F_1 & \xrightarrow{\quad} & X \\ \uparrow p & & \downarrow p_1 & \searrow q & \\ \Phi(X) & \xrightarrow{\quad} & \Phi_1(X) & & \end{array}$$

It is easily seen that  $qip = \Phi^{-1}$ ,  $p_1 i p = j$  and that the inverse-image of any point of  $X$  under  $q$  is acyclic. Hence by the Vietoris mapping theorem  $h_{q,m}^{n-1}$  is an isomorphism and if the homomorphism  $h_{\Phi^{-1},m}^{n-1} =$

$h_{q,m}^{n-1} h_{i,m}^{n-1} h_{p,m}^{n-1}$  is trivial then  $h_{i,m}^{n-1} h_{p,m}^{n-1}$  is also. Thus the homomorphism  $h_{j,m}^{n-1} = h_{p,m}^{n-1} h_{i,m}^{n-1} h_{p,m}^{n-1}$  is trivial and the theorem follows at once from the lemma.

Applications. a) Let  $MCE_n$  be a compact  $(n-1)$ -dimensional manifold. Suppose  $M$  is a fibre space with the fibre  $Y$  of dimension  $>0$ , the basis  $X$ , the projection  $p$  (see [6], § 1.1). For the family  $\mathcal{F}=\{X, E_n, p^{-1}\}$  we have  $\bigcup_m \mathfrak{P}_m(\mathcal{F}) \subset \mathfrak{S}(\mathcal{F})$ .

For in this case  $\dim X < n-1$ , hence  $X$  is acyclic mod  $m$  in dimension  $n-1$  for every  $m$ .

b) Let  $M \subset E_n$  be a compact set and  $f$  its continuous mapping onto a space  $X$  acyclic mod  $m$  in the dimension  $n-1$ . For the family  $\mathcal{F} = \{X, E_n, f^{-1}\}$  we have  $\mathfrak{P}_m(\mathcal{F}) \subset \mathfrak{S}(\mathcal{F})$ .

c) Let  $M \subset E_n$  be an  $(n-1)$ -dimensional pseudomanifold and  $T$  the simplicial complex of its triangulation. Let  $g: M \rightarrow M$  be a continuous involution on  $M$  (i. e.  $gg(x)=x$ ) without fixed points and permuting the simplexes of  $T$ . Denote by  $M^*$  the space obtained from  $M$  by identification of points  $x$  and  $g(x)$  and let  $f: M \rightarrow M^*$  be the identification mapping. For the family  $\mathcal{F}=\{M^*, E_n, f^{-1}\}$  we have  $\mathfrak{P}_2(\mathcal{F}) \subset \mathfrak{S}(\mathcal{F})$ .

To prove this, denote by  $\gamma$  the generator of  $H^{n-1}(M, \mathbb{G}_2)$ . The generator  $\gamma$  is represented by the chain of all simplexes of  $M$ , each with coefficient 1. Hence  $f(\gamma)$  consists of all simplexes of  $M^*$  each with coefficient 2. Thus  $f(\gamma) \sim 0$  in  $M^*$  mod 2. Hence  $h_{f_2}^{n-1}$  is trivial.

This last theorem will be generalized in a forthcoming note by A. Kosiński.

**4. The general case.** Let  $\mathcal{F}=\{X, E_n, \phi\}$  be a family and let  $F$  be its graph. Denote the projection of  $F$  onto  $X$  by  $f_1$ , into  $E_n$  — by  $f_2$ .

**THEOREM 2.** *If the homomorphism  $h_{f_1,m}^{n-1}$  is trivial and  $h_{f_2,m}^{n-1}$  is a homomorphism onto the corresponding group of  $\Phi(X)$  then  $\mathfrak{P}_m(\mathcal{F}) \subset \mathfrak{S}(\mathcal{F})$ .*

The proof differs very little from that of Theorem 1 (which is a special case of Theorem 2) and will be omitted.

Applications. a) Consider a family of great  $(n-k-1)$ -dimensional spheres orthogonal to a given  $k$ -dimensional great sphere  $S$  ( $k < n-1$ ) on the  $(n-1)$ -sphere  $S_{n-1} \subset E_n$ . Any such sphere intersects  $S$  in two antipodal points and distinct spheres intersect  $S$  in distinct pairs of points. Denote by  $P_k$  the projective  $k$ -dimensional space obtained from  $S$  by identification of antipodal points. Let  $i: S \rightarrow P_k$  be the identification mapping. Define the family  $\mathcal{F}=\{P_k, E_n, \Phi\}$  as follows:  $\Phi(x)$  = the  $(n-k-1)$ -dimensional great sphere orthogonal to  $S$  and intersecting  $S$  in  $i^{-1}(x)$ . Then  $\mathfrak{P}_m(\mathcal{F}) \subset \mathfrak{S}(\mathcal{F})$ .

Consider namely the graph  $F$  of  $\mathcal{F}$ . The set  $F$  is an  $(n-1)$ -dimensional manifold (it is easily seen that  $F=S_{n-k-1} \times P_k$ ). Since  $k < n-1$  the ho-

homomorphism  $h_{f_1, m}^{n-1}$  is trivial for any  $m$ . Since  $f_2$  maps  $F$  onto  $S_{n-1}$  with degree 1 it follows that  $h_{f_2, m}^{n-1}$  is a homomorphism onto.

b) Let  $M_{n, k}$  be the Grassman manifold of all (unoriented)  $k$ -dimensional planes through the origin of  $E_n$  (see [6], § 7.9). Let  $S_{n-1}$  be the unit sphere of  $E_n$ . If  $x \in M_{n, k}$  represents the plane  $\pi$ , then let  $\varphi(x)$  be the intersection of  $\pi$  and  $S_{n-1}$ . Let  $\mathcal{F} = \{M_{n, k}, E_n, \Phi\}$ . It follows immediately from the preceding example that if  $k > 1$ , then  $\bigcup_m \mathfrak{P}_m(\mathcal{F}) \subset \mathfrak{S}(\mathcal{F})$ . (The case  $k=1$  was investigated in example c) in § 3).

### 5. Common prolongation of two families.

**THEOREM 3.** Let  $\mathcal{F} = \{X, E_n, \Phi\}$  be a simple family, let  $\mathcal{F}_1 = \{X, E_n, \Phi_1\}$  be a family with field acyclic mod  $m$  in the dimension  $n-1$  and let  $f$  be the projection of the graph  $F_1$  of  $\mathcal{F}_1$  onto  $X$ . Suppose that  $h_{f, m}^{n-1}$  is a homomorphism onto. Then  $\mathfrak{P}_m(\mathcal{F}) \cap \mathfrak{P}_m(\mathcal{F}_1) \subset \mathfrak{S}(\mathcal{F})$ .

**Proof.** Let  $\mathcal{F}_2 = \{X, E_n, \Phi_2\}$  be a common prolongation of  $\mathcal{F}$  and  $\mathcal{F}_1$  acyclic mod  $m$ . Let  $F, F_1, F_2$  be the corresponding graphs,  $p$  — the projection of  $F_2$  onto  $X$ ,  $q$  — the projection of  $F_2$  onto  $\Phi_2(X)$ . Since  $\mathcal{F}$  is simple, the mapping  $q$  on  $F$  is a homomorphism. Let  $\gamma$  be a true convergent  $(n-1)$ -dimensional cycle mod  $m$  in  $\Phi(X)$  and let  $\alpha$  be a cycle in  $F_1$  such that  $p(\alpha) \sim pq^{-1}(\gamma)$  in  $X$ . The Vietoris mapping theorem implies that  $\alpha \sim q^{-1}(\gamma)$  in  $F_2$ , hence  $q(\alpha) \sim \gamma$  in  $\Phi_2(X)$ . But  $q(\alpha)$  is a cycle in  $\Phi_1(X)$  hence  $q(\alpha) \sim 0$  in  $\Phi_1(X)$  and this implies  $\gamma \sim 0$  in  $\Phi_2(X)$ . The theorem itself follows then from the lemma of 2.

**Applications.** a) Let  $\mathcal{F} = \{X, E_n, \Phi\}$  be a simple family and let  $\mathcal{F}_1 = \{X, E_n, \Phi_1\}$  be a family acyclic mod  $m$  with field acyclic mod  $m$  in the dimension  $n-1$ . Then  $\mathfrak{P}_m(\mathcal{F}) \cap \mathfrak{P}_m(\mathcal{F}_1) \subset \mathfrak{S}(\mathcal{F})$ .

b) Let  $\mathcal{F} = \{X, E_n, \Phi\}$  be a simple family and let  $\mathcal{F}_1 = \{X, E_n, \Phi_1\}$  be a family with the field acyclic mod  $m$ . Suppose, moreover, that there exists a mapping  $f: X \rightarrow \Phi_1(X)$  satisfying  $f(x) \in \Phi_1(x)$  for every  $x \in X$ . Then  $\mathfrak{P}_m(\mathcal{F}) \cap \mathfrak{P}_m(\mathcal{F}_1) \subset \mathfrak{S}(\mathcal{F})$ .

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## A Remark on the Mixing Theorem

• by  
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*Presented by H. STEINHAUS on April 25, 1955*

Let  $(X, B, m)$  be a  $\sigma$ -measure space with  $m(X)=1$ . We suppose that a fixed transformation  $T$  of  $X$  into itself is measurable and measure-preserving (i. e. if  $E \in B$ , then the inverse image  $T^{-1}E \in B$  and  $m(T^{-1}E) = m(E)$ ). As usual, we say that  $T$  is *indecomposable*, if every almost  $T$ -invariant set  $E$  (i. e. such that  $m((E - T^{-1}E) + (T^{-1}E - E)) = 0$ ) is of measure zero or one. Obviously, a transformation  $T$  is indecomposable if every almost  $T$ -invariant function  $f$  (i. e. such that  $f(Tx) = f(x)$  almost everywhere)\*) is constant a. e.

$T$  is called *weakly mixing* (cf. Hopf [1]) if for any  $E, F \in B$

$$\lim_{j \text{ non } \in N} m(E \cdot T^{-j}F) = m(E)m(F),$$

where  $N$  is a suitable sequence of density zero.

Every weakly mixing transformation  $T$  is indecomposable.

The following equivalence is known for 1-1 transformations:

THEOREM. *Weak mixing is equivalent to each of the following conditions:*

(a) *The square of  $T$ :*

$$T \times T(x, y) = (Tx, Ty)$$

*is indecomposable with respect to the direct product measure  $m \times m$ .*

(b) *The unique proper function:*

$$f(Tx) = \lambda f(x) \quad (\lambda - \text{complex})$$

*is the function  $f(x) = \text{const.}$*

The purpose of this paper is to prove this theorem without the hypothesis that  $T$  is 1-1.

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\*) In the sequel, the equality sign between two functions will always denote equality a. e.

It suffices to show that (b) implies (a), because in the known proofs of the remaining implications (see Hopf [1]) this hypothesis is not essential.

Assume that the transformation  $T \times T$  is decomposable and let  $\chi(x, y)$  denote the characteristic function of an almost invariant set  $E \subset X \times Y$  with  $0 < m \times m(E) < 1$ .

It is easy to see that one of the functions  $\chi(x, y) \pm \chi(y, x)$  is not constant a. e. We set respectively

$$K(x, y) = \chi(x, y) + \chi(y, x)$$

or

$$K(x, y) = i[\chi(x, y) - \chi(y, x)].$$

We have

$$(1) \quad K(y, x) = \bar{K}(x, y) \quad \int \int |K(x, y)|^2 dx dy < \infty$$

$$(2) \quad K(Tx, Ty) = K(x, y).$$

Further we treat  $K$  as the kernel of the integral equation

$$\mu \int K(x, y) f(y) dy = f(x)$$

in the space  $L^2(m)$  and, in view of (1), we can apply Hilbert-Schmidt theorems (see e. g. Riesz-Nagy [2], p. 239–242).

Let  $L^2\mu$  be the subspace of  $L^2(m)$  consisting of all proper functions corresponding to the proper value  $\mu$ .

If a function  $f(x)$  belongs to  $L^2\mu$  then the function  $f(Tx)$  also does. In fact

$$f(Tx) = \mu \int K(Tx, y) f(y) dy = \mu \int K(Tx, Ty) f(Ty) dy = \mu \int K(x, y) f(Ty) dy.$$

Obviously,  $\int |f(Tx)|^2 dx = \int |f(x)|^2 dx$ . Thus, the correspondence between functions:  $f(x) \rightarrow f(Tx)$  is a linear isometric transformation of  $L^2\mu$  onto itself ( $L^2\mu$  is of finite dimension). Then, there is an orthonormal basis of  $L^2\mu$ , consisting of the proper functions  $f_1, f_2, \dots, f_n$  of the transformation  $T$ :

$$f_j(Tx) = \lambda_j f_j(x) \quad |\lambda_j| = 1 \quad j = 1, 2, \dots, n.$$

Since  $K$  is not constant a. e., there is a proper value  $\mu$  and a function  $f_j$  also not constant a. e.

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## A Proof of $\varepsilon$ -Theorems

by

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*Presented by K. KURATOWSKI on April 30, 1955*

The aim of this paper \*) is to outline the idea of a simple algebraic proof of the well-known  $\varepsilon$ -theorems \*\*). The proof is to appear in *Fundamenta Mathematicae* (vol. 43) in a paper under the same title.

The method applied is the same as the method used in the previous papers, e. g. in *Algebraic models of axiomatic theories* cited hereafter as [A M] (see [4]). The knowledge of [A M] is here assumed.

The proof sketched in this note is valid also for non-enumerable theories. It is known that the algebraic proof of the Skolem-Gödel theorem for non-enumerable open theories can be carried out in a very simple way (see [3] or [5] and [6]). The transition to the case of arbitrary theories may be accomplished by the use of the  $\varepsilon$ -theorem and was applied by Łoś [3]. Thus, Malcev's theorem i. e. the Skolem-Gödel theorem for non-enumerable theories may be proved in a simple manner, different from that of Henkin [1].

It should also be noted that the suggested proof of  $\varepsilon$ -theorems can be generalized for theories formalized on the basis of certain non-classical functional calculi.

Let  $T(\mathfrak{A})$  \*\*\* be an elementary theory (with the set  $\mathfrak{A}$  of axioms) formalized on the basis of the functional calculus  $T(\Lambda)$  \*\*\*\*). We assume that the following symbols are the primitive signs of  $T(\mathfrak{A})$ : *individual variables*  $x_1, x_2, \dots$ ; *individual constants*  $a_1, a_2, \dots$ ; *functors with  $l$ -arguments*  $f_1^l, f_2^l, \dots$  (i. e. symbols for functions from individuals to individuals); *predicates with  $k$ -arguments*  $F_1^k, F_2^k, \dots$ ; *sentential operators*  $+, \cdot, \rightarrow, -$ ; *quantifiers*  $\prod, \sum$  ( $i=1, 2, \dots$ ). The set  $Cn(\mathfrak{A})$  of all theorems of  $T(\mathfrak{A})$  consists

\*) Presented at the Polish Mathematical Society on March 11, 1955.

\*\*) See Hilbert-Bernays [2]. Another simple proof of the first  $\varepsilon$ -theorem was given by Łoś [3].

\*\*\* For the description of the theory  $T(\mathfrak{A})$  see [A M], p. 298.

\*\*\*\*)  $\Lambda$  denotes always the empty set.

of all  $\alpha \in \mathfrak{A}$ , of all substitutions of tautologies of the sentential calculus and of all other formulas derivable from the above mentioned one, by the use of the known rules of inference.

If the set  $\mathfrak{A}$  contains only open formulas, we shall distinguish the set  $Cn_0(\mathfrak{A})$  ( $Cn_1(\mathfrak{A})$ ) of theorems formally proved without using the rules of inference for the quantifiers (and without using the rule of substitution for individual variables). The theory with the set  $Cn_0(\mathfrak{A})$  of theorems will be denoted by  $T_0(\mathfrak{A})$ . In this case let  $\bar{\mathfrak{A}}$  denote the smallest class of formulas of  $T(\mathfrak{A})$  containing  $\mathfrak{A}$  and closed with respect to substitutions. It is known that:

$$1. Cn_1(\bar{\mathfrak{A}}) = Cn_0(\mathfrak{A}).$$

2. If  $\alpha \in Cn_1(\bar{\mathfrak{A}})$  then there exist  $\beta_1, \dots, \beta_n \in \mathfrak{A}$  such that  $\beta_1 \cdot \dots \cdot \beta_n \rightarrow \alpha \in Cn(\wedge)$  (i. e.  $\beta_1 \cdot \dots \cdot \beta_n \rightarrow \alpha$  is provable in  $T(\wedge)$ ).

Given a theory  $T(\mathfrak{A})$  we shall treat each formula  $\alpha$  of this theory as an algebraic functional  $(J, B)\Phi_\alpha^*$  defined in a domain  $J \neq \wedge$  of individuals, with values belonging to a fixed complete Boolean algebra  $B$ . Instead of  $(J, B)\Phi_\alpha$  we shall also write  $(J, B)\Phi(\alpha)$ .

Let

$$(*) \quad a_i = j_i \in J, \quad f_n^l = \tau_n^l, \quad F_m^k = \varphi_m^k$$

(where  $\tau_n^l$  are  $l$ -argument functions defined on  $J$  with values in  $J$  and  $\varphi_m^k$  are  $k$ -argument functions defined on  $J$  with values in  $B$ ) be a fixed system of valuations of all individual constants, functions and predicates of  $T(\mathfrak{A})$ . This system will be denoted by  $\mathfrak{M} = [\{j_i\}, \{\tau_n^l\}, \{\varphi_m^k\}]$  and will be called an algebraic pseudomodel of  $T(\mathfrak{A})$  in  $J$  and  $B$ .  $\mathfrak{M}$  is said to be an algebraic generalized model of  $T(\mathfrak{A})$  ( $T_0(\mathfrak{A})$ ) if for every  $\alpha \in \mathfrak{A}$ ,  $(\mathfrak{M})\Phi_\alpha = 1$ , i. e. if the value of  $(J, B)\Phi_\alpha$  is equal to the unit of  $B$  for the values of its arguments fixed by  $(*)$  and for any values of  $x_i (i=1, 2, \dots)$ .

It is known (see [A M] 3.5) that

3. If  $\alpha \in Cn(\mathfrak{A})$  ( $Cn_0(\mathfrak{A})$ ) then  $(\mathfrak{M})\Phi_\alpha = 1$  in every generalized model  $\mathfrak{M}$  in every domain  $J \neq \wedge$  and every complete Boolean algebra  $B$ . In particular if  $\alpha \in Cn(\wedge)$  then  $(\mathfrak{M})\Phi_\alpha = 1$  in every pseudomodel  $\mathfrak{M}$ .

The following theorem is a consequence of Theorem 3.6 proved in [A M].

4. Given a theory  $T(\mathfrak{A})$  ( $T_0(\mathfrak{A})$ ), there exists a functionally free generalized algebraic model  $\mathfrak{R}$  ( $\mathfrak{R}_0$ ) of  $T(\mathfrak{A})$  ( $T_0(\mathfrak{A})$ ), i. e. with the following property: for any formula  $\alpha$ ,  $\alpha \in Cn(\mathfrak{A})$  ( $\alpha \in Cn_0(\mathfrak{A})$ ) if and only if,  $(\mathfrak{R})\Phi_\alpha = 1$  ( $(\mathfrak{R}_0)\Phi_\alpha = 1$ ).

\*) For the description of the functional  $(J, B)\Phi_\alpha$  see [A M], p.297.

5. *The first  $\varepsilon$ -theorem \**. Given an open formula  $a$  of a theory  $T(\mathfrak{A})$  all of whose axioms are open formulas, if  $a \in Cn(\mathfrak{A})$  then  $a \in Cn_0(\mathfrak{A})$ .

Indeed, suppose that  $a \in Cn_0(\mathfrak{A})$ . Then by 4,  $(\mathfrak{R}_0)\Phi_a = 1$ . But  $\mathfrak{R}_0$  is also an algebraic generalized model of  $T(\mathfrak{A})$ . Hence, on account of 3,  $a \in Cn(\mathfrak{A})$ .

In the sequel let  $T(\mathfrak{A})$  be a theory, all of whose axioms  $a_\varrho \in \mathfrak{A}(\varrho \in R)$  are closed formulas in the prenex normal form. Using the known *Skolem method* (see [2]) of elimination of quantifiers it is possible to pass from  $T(\mathfrak{A})$  to a theory  $T^*(\mathfrak{A}^*)$  with the set  $\mathfrak{A}^*$  of open formulas, and with new primitive signs of annexed individual constants and functors. Then  $T^*(\wedge)$  denotes the functional calculus, being the basis for the formalization of  $T^*(\mathfrak{A}^*)$ . It is easy to see that

6. *Given a formula  $a$  of  $T(\mathfrak{A})$ , if  $a$  is provable in  $T^*(\wedge)$ , then it is also provable in  $T(\wedge)$ .*

For any  $a_\varrho \in \mathfrak{A}$ , we shall denote by  $\gamma_\varrho$  the arbitrary substitution of the formula  $a_\varrho^* \in \mathfrak{A}^*$  arising from  $a_\varrho$  by the elimination of quantifiers.

Given a pseudomodel  $\mathfrak{M}$  of  $T(\mathfrak{A})$  in  $J$  and  $B$ , we may extend it to a pseudomodel  $\mathfrak{M}^*$  of  $T^*(\mathfrak{A}^*)$  in  $J$  and  $B$ , fixing a valuation for all annexed signs.

7. *Given a pseudomodel  $\mathfrak{M}$  of the theory  $T(\mathfrak{A})$  and formulas  $\gamma_{e_1}, \dots, \gamma_{e_r}$  if for every extension  $\mathfrak{M}^*$  of the pseudomodel  $\mathfrak{M}$ ,  $(\mathfrak{M}^*)\Phi(\gamma_{e_1} \dots \gamma_{e_r}) = 0$  identically, then  $(\mathfrak{M})\Phi(a_{e_1} \dots a_{e_r}) = 0$ .*

The second  $\varepsilon$ -theorem is equivalent (see [2]) with the following.

8. *The consistency of a theory  $T(\mathfrak{A})$  implies the consistency of  $T^*(\mathfrak{A}^*)^{**}$ .*

Suppose that  $T^*(\mathfrak{A}^*)$  is inconsistent. Then for an open formula  $a$  of  $T(\mathfrak{A})$  holds  $a, -a \in Cn(\mathfrak{A}^*)$ . On account of 5,  $a, -a \in Cn_0(\mathfrak{A}^*)$ .

Hence, by 1,  $a, -a \in Cn_1(\mathfrak{A}^*)$ . Consequently, by 2 there exist  $\gamma_{e_1}, \dots, \gamma_{e_r} \in \mathfrak{A}^*$  such that  $\gamma_{e_1} \dots \gamma_{e_r} \rightarrow a, -a$  is provable in  $T^*(\wedge)$ . Let  $\mathfrak{N}^*$  be a functionally free model of  $T^*(\wedge)$ , and let  $\mathfrak{M}$  be the pseudomodel of  $T(\mathfrak{A})$  such that  $\mathfrak{N}^*$  is an extension of  $\mathfrak{M}$ . It follows from 3 that in every pseudomodel  $\mathfrak{M}^*$  of  $T^*(\mathfrak{A}^*)$ , being an extension of  $\mathfrak{M}$ ,  $(\mathfrak{M}^*)\Phi(\gamma_{e_1} \dots \gamma_{e_r} \rightarrow a, -a) = 1$ . Consequently  $(\mathfrak{M}^*)\neg(\gamma_{e_1} \dots \gamma_{e_r}) = 0$ . On account of 7,  $(\mathfrak{M})\Phi(a_{e_1} \dots a_{e_r}) = 0$ . That is  $(\mathfrak{M})\neg(a_{e_1} \dots a_{e_r} \rightarrow a, -a) = 1$ . Since  $a_{e_1}, \dots, a_{e_r}, a$  are formulas of  $T(\mathfrak{A})$ , we have  $(\mathfrak{M}^*)\Phi(a_{e_1} \dots a_{e_r} \rightarrow a, -a) = 1$ .  $\mathfrak{N}^*$  being the functionally free model, we infer that  $a_{e_1} \dots a_{e_r} \rightarrow a, -a$  is provable in  $T^*(\wedge)$ , and by 6, in  $T(\wedge)$  too. Consequently  $a, -a \in Cn(\mathfrak{A})$ .

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\*) This theorem can be proved in a similar way for the non-classical theories considered in [A M], in particular, based on the *positive, minimal, intuitionistic* and *modal* logic.

\*\*) This theorem can be analogously proved for some non-classical theories, e. g. for the theories based on *intuitionistic* logic. In this case, theorem 8 may also be obtained from an unpublished result of Łoś.

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## The Diffusion of Light through a Scattering Layer of Great Optical Thickness

by

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*Communicated by H. NIEWODNICZAŃSKI at the meeting of March 28, 1955*

The present note deals with a certain problem concerning the diffusion of light through a plane-parallel scattering layer of great optical thickness. A uniform layer of clouds illuminated on the upper boundary by parallel sun rays is an example of such a layer in Geophysics. Terrestrial clouds have very small absorption in the visual region of the spectrum; they represent an almost ideal case of pure scattering. Let  $\tau$  — the optical thickness — vary from  $\tau=0$  on the upper boundary, to  $\tau=\tau_1$  on the lower. Exact formulae, giving for arbitrary  $\tau_1$  the intensity of transmitted and reflected radiation, are ill-adapted for numerical applications — particularly for great  $\tau_1$ . Moreover, they do not give any possibility of getting a clear idea of the proportion in which for a given (great)  $\tau_1$  the light is divided into a reflected and transmitted part. In the present note an exact asymptotic formula is given for the total flux of the light transmitted through a thick scattering layer in the case of an isotropic or simple elongated scattering indicatrix. For the arbitrary shape of the indicatrix a general approximate solution is given with an arbitrary high degree of approximation.

Let the scattering indicatrix be given by the phase function  $p$

$$(1) \quad p(\cos \theta) = \sum_{l=0}^N \tilde{\omega}_l P_l(\cos \theta),$$

where  $\theta$  denotes the angle between the directions of the incident and scattered ray;  $\tilde{\omega}_0, \tilde{\omega}_1, \dots, \tilde{\omega}_N$  are constants;  $P_l$  is the Legendre polynomial of degree  $l$ . For the case of pure scattering,  $\tilde{\omega}_0=1$ . Let, further,  $\mu$  denote the cosine of the angle between the direction of the pencil of diffuse radiation and the outward normal to the layer,  $\varphi$  — the azimuth of this pencil. Let the direction of the parallel beam of (solar) rays illuminating the layer be specified by —  $\mu_0, \varphi_0 (\mu_0 > 0)$ ; let the flux of this radiation per

unit area, normal to the direction of propagation, be on the upper boundary  $\pi F$ . If the intensity of the diffuse radiation travelling in the direction  $\mu, \varphi$  at the optical depth  $\tau$  be expanded in the form

$$I(\tau, \mu, \varphi) = \sum_{m=0}^N I^{(m)}(\tau, \mu) \cos m(\varphi - \varphi_0),$$

we can see that the net flux of radiation  $F(\tau)$  defined by the equation

$$F(\tau) = \int I \mu d\omega,$$

depends only on  $I^{(0)}(\tau, \mu)$  ( $d\omega$  is an element of solid angle and the integration is to be performed over the whole sphere). In the case of pure scattering ( $\tilde{\omega}_0 = 1$ ) the problem admits the flux integral

$$F(\tau) = \pi F \mu_0 (e^{-\tau/\mu_0} + c),$$

where  $c$  is constant; determination of the flux of diffuse radiation transmitted through the layer is reduced in this way to determination of  $c$ .

In Chandrasekhar's method, employed by the present writer, we use, when solving the equation of radiative transfer, Gauss's quadrature formula for the integral figuring in this equation; we replace  $I(\tau, \mu)$  (we omit the superscript  $^{(0)}$ ) by  $2n$  functions  $I_i(\tau, \mu_i)$  taken for  $2n$  directions  $\mu_i$   $i = \pm 1, \dots, \pm n$ ;  $\mu_{-i} = -\mu_i$  corresponding to zeros of the Legendre polynomial  $P_{2n}$ . This is the so-called  $n$ -th approximation. In the case when the phase function  $p$  is given by the simple expression  $p = 1 + \tilde{\omega}_1 \cos \theta$  we have

$$(2) \quad I_i = \frac{1}{4} F \left\{ \sum_{a=-n+1}^{n-1} \frac{L_a e^{-k_a \tau}}{1 + \mu_i k_a} + L_0 \left[ (1 - \frac{1}{3} \tilde{\omega}_1) \tau + \mu_i \right] + L_n + e^{-\tau/\mu_i} \frac{H(\mu_0) H(-\mu_0)}{1 + \mu_i/\mu_0} \right\};$$

$L_{\pm a}$ ,  $a = 1, \dots, n-1$ ;  $L_0, L_n$  are  $2n$  constants of integration, which must be found from the boundary conditions stating that there is no diffuse radiation entering the upper ( $\tau = 0$ ) boundary and no such radiation entering the lower ( $\tau = \tau_1$ ) boundary

$$(3) \quad I_{-i} = 0 \quad \text{for} \quad \tau = 0; \quad i = 1, \dots, n;$$

$$(3 \text{ bis}) \quad I_{+i} = 0 \quad \text{for} \quad \tau = \tau_1; \quad i = 1, \dots, n;$$

$k_{\pm a}$  ( $a = 1, \dots, n-1$ ) are non-vanishing roots, which occur in pairs, of the characteristic equation

$$1 = \sum_{i=1}^n \frac{a_i}{1 - \mu_i^2 k^2},$$

where  $a_i$  are weights appropriate for Gauss's quadrature formula and

$$H(\mu) = \frac{1}{\mu_1 \dots \mu_n} \frac{(\mu + \mu_1) \dots (\mu + \mu_n)}{(1 + k_1 \mu) \dots (1 + k_n \mu)},$$

The formulae written above were given by Chandrasekhar [1].

Applying Gauss's quadrature formula for the determination of  $F(\tau)$ , we find

$$F(\tau) = \pi F \mu_0 \left( e^{-\tau \mu_1} + \frac{L_0}{3 \mu_0} \right).$$

This formula holds good also in the case where the expansion of  $p$  is not limited to the two lowest terms. The flux of radiation emerging from the lower boundary is  $F(\tau_1)$ ; to compute it we must find  $L_0$ . Determination of the constant  $L_0$  from equations expressing the boundary conditions becomes simpler for great  $\tau_1$ ; we can omit then in these equations terms of the order  $e^{-\tau_1}$  as compared with terms of the order  $e^0$ . In this way we find

$$(4) \quad L_0 = \frac{W_{\mu_1}^{(n)} / W_1^{(n)}}{(1 - \frac{1}{3} \tilde{\omega}_1) \tau_1 + 2 W_{\mu}^{(n)} / W_1^{(n)}},$$

where in the first row of the determinant  $W_1^{(n)}$  there are 1's and in the row  $a+1$  ( $a=1, \dots, n-1$ )  $1/(1 - \mu_i k_a)$ ,  $i=1, \dots, n$ ;  $W_{\mu}^{(n)}$  and  $W_{\mu}^{(n)}$  are determinants which are obtained from  $W_1^{(n)}$  by replacing the first row in it by

$$\frac{H(\mu_0)H(-\mu_0)}{1 - \mu_1/\mu_0}, \dots, \frac{H(\mu_0)H(-\mu_0)}{1 - \mu_n/\mu_0} \quad \text{or} \quad \mu_1, \dots, \mu_n$$

respectively. When the expansion (1) of  $p$  is not curtailed at the second term the shape of formula (4) remains the same but in the determinants  $W_1^{(n)}$ ,  $W_{\mu}^{(n)}$ ,  $W_{\mu}^{(n)}$  there appear now certain rational functions of  $k_a$  or of  $\mu_0$  which figure in the expression which in this case replaces (2). The essential conclusion from (4) is that for an arbitrarily high approximation and for an arbitrary shape of the scattering indicatrix the flux of diffuse radiation transmitted through a scattering layer of great optical thickness  $\tau_1$  depends on  $\tau_1$  and  $\tilde{\omega}_1$  only through the product  $(1 - \frac{1}{3} \tilde{\omega}_1) \tau_1$  in the way disclosed by (4).

Returning to the case of the simple phase function  $1 + \tilde{\omega}_1 \cos \theta$ , we can significantly simplify expression (4) by passing from  $n$  to  $\infty$ . After some lengthy algebra we find that

$$W_{\mu}^{(n)} / W_1^{(n)} = \mu_1 + \mu_2 + \dots + \mu_n - \left( \frac{1}{k_1} + \frac{1}{k_2} + \dots + \frac{1}{k_{n-1}} \right);$$

this is ([1], p. 79) the  $n$ -th approximation of the limit  $q(\infty)$  to which Hopf's function  $q(\infty)$  tends in the transfer problem for stellar atmospheres in local thermodynamic equilibrium;  $q(\infty) = 0.710446 \dots$ . Further it appears that

$$W_{\mu_1}^{(n)} / W_1^{(n)} = -\mu_0 \frac{H(\mu_0)}{k_1 \dots k_{n-1} \mu_1 \dots \mu_n};$$

the product in the denominator of the right-hand side is equal  $\frac{1}{3}$  ([1], p. 74).

The exact — in the “infinite approximation” — shape of the function  $H$ , which characterizes the limb darkening in the photospheric problem, is given by several authors ([1] p. 125, last column of table XL) in tabular form. Finally we obtain instead of (4) an exact asymptotic formula

$$(5) \quad \frac{L_0}{3\mu_0} = - \frac{H(\mu_0)/\sqrt{3}}{(1 - \frac{1}{3}\tilde{\omega}_1)\tau_1 + 2q(\infty)}.$$

When  $e^{-\tau_1\mu_0}$  can be omitted as compared with  $L_0/(3\mu_0)$ , formula (5) gives directly the fraction of light transmitted diffusely. For the single act of scattering, the net flux with respect to the plane normal to the direction of the incident beam depends only on  $\tilde{\omega}_1$ ; we may therefore expect that formula (5) will give a good approximation also in the case, where the expansion of  $p$  is not limited to the two lowest terms only. Some computations made by the writer with the aid of the generalized formula (4) confirm this expectation.

For terrestrial clouds, formula (5) shows in a clear way the dependence of the illumination on  $\tilde{\omega}_1$  and  $\tau_1$  and can serve as one of the bases for the determination of these parameters by observation. For the average size of water drops in a cloud,  $\frac{1}{3}\tilde{\omega}_1$  approaches 1; the smallness of the coefficient of  $\tau_1$  in (5) and (4) explains the relative smallness of the variations in illumination by a cloudy sky, in spite of very large variations in the thickness of the clouds; this smallness explains also why, in spite of its enormous surface brightness, the disc of the sun is invisible through a cloud transmitting a considerable fraction (e.g. 20%) of incident light.

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# On the Proofs of "Backward" Uniqueness for Some Non-Conservative Fields Describable by Differential Equations of the Hyperbolic Type

by

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*Communicated by A. RUBINOWICZ at the meeting of March 28, 1955*

1. The proofs of uniqueness for linear differential equations of the hyperbolic type are based on the assumption of continuity of the physical phenomena described by these equations (e. g. law of conservation of energy, equation of continuity for the probability current). Theorems on the uniqueness of the solution (uniqueness meaning that there exists at most one solution), as usually formulated for hyperbolic type equations or systems thereof, besides their mathematical value, have also a certain physical interpretation. Namely, if the initial conditions are prescribed within a bounded region, then the uniqueness of the solution of Cauchy's problem means that the velocity of propagation of "signals" is finite.

Theorems on the uniqueness of the solution of the problem of initial value were first formulated by Zaremba [1] and Rubinowicz [2], [3]. Their ideas were developed by other authors [4], [5]. Plebański [6] has recently formulated two theorems on uniqueness, valid for a wide class of differential equations in mathematical physics. These theorems will be briefly described in section 3. In the present paper, the results obtained by Plebański have been extended to some equations, such that the equation of continuity  $I'_{,\nu} + Q = 0$  follows from them as a consequence (see section 4). This makes possible the proof of "backward uniqueness" for Maxwell's macroscopic equations and for the equations of the scalar fields (see section 5).

2. In the present paper, the usual notations of the theory of relativity will be used, repeated upper and lower index meaning a sum from 0 to 3 (Greek indices) or from 1 to 3 (Latin indices),  $x^0$  — time co-ordinate;  $x^1, x^2, x^3$  — space co-ordinates.  $\varphi_{,\alpha}$  designates  $\frac{\partial \varphi}{\partial x^\alpha}$  and the symbol  $d_k \tau$  in the integrand denotes integration over a  $k$ -dimensional continuum.

$FA$  denotes the boundary of the region  $A$ . We shall deal with systems of linear partial differential equations ("the field equations") such that the characteristic quadratic form

$$(1) \quad A[\vec{\xi}] = a^{\alpha\beta} \xi_\alpha \xi_\beta,$$

where  $a^{\alpha\beta} = a^{\alpha\beta}(x^\nu)$  satisfies, in the region under consideration, the following conditions:

$$(2.1) \quad a^{00} > 0, \quad (2.2) \quad a^{0k} = 0, \quad (2.3) \quad a^{\alpha\beta} = a^{\beta\alpha},$$

$$(2.4) \quad a^{kl} \xi_k \xi_l < 0, \quad \text{if} \quad \vec{\xi} \neq 0.$$

Let  $R$  denote a bounded region of the three-dimensional continuum. We assume for simplicity that  $R$  lies on a hyperplane  $x^0 = 0$ . Let us consider a set of characteristic cones (we understand the characteristic cone as a surface formed by a set of bicharacteristics passing through a definite point) with vertices on a two-dimensional surface  $FR$ . We denote by  $\Omega$  the set of such points  $x^\nu$  of a four-dimensional continuum, so that each of them can be connected with an arbitrary point in  $R$  by means of a line which will not cross any of the characteristic cones. The set of points belonging to  $\Omega$  so that  $0 < x^0 < x_k^0$  (or  $x_k^0 < x^0 < 0$ , if  $x_k^0 < 0$ ), is denoted by  $\Omega(x_k^0)$ .  $R(x_k^0)$  is the common part of  $\Omega$  and the hyperplane  $x^0 = x_k^0$ . Further:  $T(x_k^0) = F\Omega(x_k^0) - R - R(x_k^0)$ . We chose the direction of the normal unit vector  $\vec{n}_\nu$  so as to have  $n_0 > 0$ .

3. The following lemma was shown by Plebański: if  $I^\nu$  is a vector field such that

$$(3) \quad I^0 \geq 0, \quad a_{\alpha\beta} I^\alpha I^\beta \geq 0; \quad \text{where} \quad (a_{\alpha\beta}) = (a^{\alpha\beta})^{-1},$$

then

$$(4) \quad \lambda = I^\alpha n_\alpha \geq 0 \quad \text{on} \quad R = R(0), \quad R(x_k^0), \quad T(x_k^0).$$

If an equation of continuity

$$(5) \quad I^\alpha_{;\alpha} + Q = 0$$

follows from the equations of the field, then integrating both sides of (5) over  $\Omega(x_k^0)$  we obtain:

$$(6) \quad \varepsilon \int_{\Omega(x_k^0)} Q d_4 \tau - \int_{R(0)} I^0 d_3 \tau + \int_{R(x_k^0)} I^0 d_3 \tau + \int_{T(x_k^0)} \lambda d_3 \tau = 0,$$

where  $\varepsilon = \text{sgn } x_k^0$ . If  $I^0|_R = 0$ , we obtain from (6) with respect to (4):

$$I^0 = 0 \quad \text{in} \quad R(x_k^0), \quad \text{if} \quad Q \geq 0, \quad x_k^0 > 0,$$

$$I^0 = 0 \quad \text{in} \quad R(x_k^0), \quad \text{if} \quad Q \leq 0, \quad x_k^0 < 0.$$

If vanishing of  $I^0$  is equivalent to vanishing of the corresponding functions

of the field, then the theorem on uniqueness follows from the above two lemmata in the known way. In the case of  $Q=0$  ("conservative field") the uniqueness of the solution can be proved in the whole region  $\Omega$ , and in particular, in  $\Omega$  (i. e. in  $\Omega(x_k^0)$  for any  $x_k^0 < 0$ ) which is the case of "backward" uniqueness.

4. The above theorems do not determine the uniqueness if the sign of  $Q$  is not constant; they also give no information concerning the behaviour of the field in  $\Omega(x_k^0)$  for  $x_k^0 > 0$  provided  $I^0|_R = 0$  in the case of  $Q \leq 0$ , and they do not determine the "backward" uniqueness in the case of  $Q \geq 0$ , which is the case of Maxwell's equations for conducting media. We shall now prove a theorem from which the "backward" uniqueness for Maxwell's macroscopic equations follows as one of the consequences.

THEOREM. *If a vector field  $I^v$ , continuous in  $\Omega$ , satisfies the conditions (3) and (5) and there exists such a constant  $M$ , that for each  $x^v \in \Omega$  there is*

$$(7) \quad |Q| \leq MI^0,$$

*then the vanishing of  $I^0$  on  $R$  implies the vanishing of  $I^0$  in  $\Omega$ .*

We shall prove this theorem for  $x_k^0 > 0$  and  $x_k^0 < 0$  simultaneously. From (6) we get

$$(8) \quad 0 \leq E(x_k^0) = \int_{R(x_k^0)} I^0 d_3 \tau - \int_{R(0)} I^0 d_3 \tau - \varepsilon \int_{\Omega(x_k^0)} Q d_4 \tau - \int_{\tau(x_k^0)} \lambda d_3 \tau.$$

Taking into account (4) we obtain

$$(9) \quad 0 \leq E(x_k^0) \leq -\varepsilon \int_{\Omega(x_k^0)} Q d_4 \tau + \int_{R(0)} I^0 d_3 \tau \leq \int_{\Omega(x_k^0)} |Q| d_4 \tau + E(0),$$

hence by (7):

$$(10) \quad 0 \leq E(x_k^0) \leq E(0) + \int_{\Omega(x_k^0)} MI^0 d_4 \tau = E(0) + \varepsilon M \int_0^{x_k^0} E(x^0) dx^0.$$

Denoting

$$\psi(x_k^0) = e^{-\varepsilon M x_k^0} \int_0^{x_k^0} E(x^0) dx^0$$

we obtain:

$$\psi'(x_k^0) = -\varepsilon M \psi + e^{-\varepsilon M x_k^0} E(x_k^0).$$

Thus (10) becomes

$$(11) \quad \psi'(x_k^0) \leq E(0) e^{-\varepsilon M x_k^0}.$$

Now let  $x_n^0$  be an arbitrary number so that  $\text{sgn } x_n^0 = \text{sgn } x_k^0$ . Integrating

both sides of inequality (11) over the interval  $(0, x_n^0)$ , if  $x_n^0 > 0$ , or over  $(x_n^0, 0)$  if  $x_n^0 < 0$ , we obtain:

$$\varepsilon[\psi(x_n^0) - \psi(0)] \leq -\frac{E(0)}{M}(e^{-\varepsilon M x_n^0} - 1)$$

and, since  $\psi(0) = 0$ , we get:

$$(12) \quad \varepsilon \int_0^{x_n^0} E(x^0) dx^0 \leq \frac{E(0)}{M}(e^{\varepsilon M x_n^0} - 1).$$

According to (12), and bearing in mind that  $\varepsilon x_n^0 = |x_n^0|$ , we obtain from (10) for an arbitrary  $x_k^0$ :

$$(13) \quad 0 \leq \int_{R(x_k^0)} I^0 d_3 \tau \leq E(0) + E(0)(e^{\varepsilon M x_k^0} - 1) = e^{M|x_k^0|} \int_R I^0 d_3 \tau.$$

Putting  $I^0|_R = 0$  into (13), we obtain proof of our theorem.

If  $I^0$  is interpreted as the density of the field energy, then (13) states that the changes of energy in  $\Omega$  are at most of an exponential nature.

Conclusion: if

1° the functions  $\varphi^A (A = 1, 2, \dots, N)$  satisfy linear differential equations with the characteristic quadratic form  $A[\vec{\xi}] = a^{\alpha\beta} \xi_\alpha \xi_\beta$ ,

2° the form  $A[\vec{\xi}]$  has the properties (2.1)–(2.4),

3° the field equations lead to the equation of continuity (5),

4° the vector field  $I^\nu$  is continuous and satisfies (3),

5° there exists a constant  $M$  satisfying (7) inside  $\Omega$ ,

6° vanishing of  $I^0$  is equivalent to vanishing of  $\varphi^A$ ,

there exists at most one solution of the field equations in  $\Omega$  satisfying on  $R$  the prescribed initial conditions.

Proof. If two solutions  $\varphi_1^A, \varphi_2^A$  existed, then in view of the linearity of the equations,  $\varphi_*^A = \varphi_1^A - \varphi_2^A$  would also be a solution satisfying the initial homogeneous conditions  $\varphi_*^A|_R = 0$ . However, the vector  $I_*^a$  corresponding to the field  $\varphi_*^A$  would vanish in  $R$ , and thus, by virtue of the theorem which has been proved, it would also vanish in  $\Omega$ . Thus it follows that  $\varphi_*^A \equiv 0$  i. e.  $\varphi_1^A = \varphi_2^A$  inside  $\Omega$ .

## 5. EXAMPLES.

### a. Maxwell's equations.

From the macroscopic equations of the electromagnetic field we can obtain a conservation principle of the form

$$(14) \quad \operatorname{div} \vec{S} + \frac{\partial W}{\partial t} = -\sigma E^2 = -Q,$$

where  $\vec{S} = \frac{c}{4\pi} \vec{E} \times \vec{H}$ ,  $W = \frac{1}{8\pi} (\varepsilon E^2 + \mu H^2)$ ;  $\varepsilon, \mu, \sigma$  are positive functions of

the point  $x^k$ , and  $\varepsilon \geq 1$ . The components of  $\vec{E}$  and  $\vec{H}$  satisfy the wave equation with the characteristic form  $\frac{\varepsilon \mu}{c^2} \xi_0^2 - \xi_1^2 - \xi_2^2 - \xi_3^2$  which is of type (2). Denoting  $(x^0, x^1, x^2, x^3) = (t, x, y, z)$ ,  $(I^0, I^1, I^2, I^3) = (W, \vec{S})$  we can write (14) in the form of (5). It can easily be proved that vector  $I^a$  satisfies the conditions (3). Assuming  $M = 8\pi \cdot \sup \sigma$ , we find (in view of  $\varepsilon \geq 1$ ) that condition (7) is satisfied. Assumptions 1°–6° are thus fulfilled and it follows that there exists at most one electromagnetic field in  $\Omega$  taking prescribed values in a bounded region  $R$ .

b. Scalar field equation.

Let us consider the equation

$$(15) \quad K[u] = (a^{\alpha\beta} u_{,\alpha})_{,\beta} + b^a u_a + cu = 0,$$

where

$$(16) \quad \begin{cases} a^{\alpha\beta} & \text{are differentiable functions satisfying (2),} \\ c \geq 0 & \text{inside } \Omega, \\ b^a & \text{are functions continuous in } \Omega. \end{cases}$$

If  $b^a = 0$ , (15) is the Euler-Lagrange equation of the following problem:

$$\delta \int_{\Omega} L d_4 \tau = 0, \quad \text{where } L = a^{\alpha\beta} u_{,\alpha} u_{,\beta} - cu^2.$$

The impulse-energy tensor

$$T_a^\beta = \delta_a^\beta L - u_{,\alpha} \frac{\partial L}{\partial u_{,\beta}} = \delta_a^\beta L - 2a^{\mu\beta} u_{,\mu} u_{,\alpha}$$

satisfies the equation

$$T_{a,\beta}^\beta = 2u_{,\alpha} b^a u_{,\beta}.$$

Defining  $I^\beta = -T_0^\beta$ , we obtain:  $I_{,\beta}^\beta = -2u_{,0} b^a u_{,\beta} = -Q$  and

$$(17) \quad I^0 = a^{00} u^2_{,0} - a^{mn} u_{,m} u_{,n} + cu^2 \geq 0.$$

If, further,  $(a_{\alpha\beta}) = (a^{\alpha\beta})^{-1}$ , then

$$(18) \quad a_{\alpha\beta} I^\alpha I^\beta = a_{00} L^2 + 4cu^2 u^2_{,0} \geq 0.$$

Denoting the upper bound of the function  $2|b^0| + |b^1| + |b^2| + |b^3|$  in  $\bar{\Omega}$  by  $M_1$  we get:

$$(19) \quad |Q| = |2u_{,0} b^a u_{,\beta}| \leq M_1 \sum_{\alpha=0}^3 u^2_{,\alpha}.$$

Let  $\kappa$  denote the smallest lower bound of the moduli of characteristic roots of the form  $A[\vec{\xi}]$ . In view of (2.1) and (2.4), it must be that  $\kappa > 0$ , and

$$(20) \quad a^{00} \xi_0^2 - a^{mn} \xi_m \xi_n \geq \kappa \sum_{\alpha=0}^3 \xi_\alpha^2.$$

Taking into account (17), (19) and (20), we get:

$$(21) \quad |Q| \leq \frac{M_1}{\kappa} (a^{00} u^2_{,0} - a^{mn} u_{,m} u_{,n}) \leq \frac{M_1}{\kappa} I^0 = MI^0.$$

It can be seen from equations (16)–(21) that in the case of equation (15) the assumptions  $1^0$ – $5^0$  of the conclusion on uniqueness are satisfied. Further, vanishing of  $I^0$  is equivalent to vanishing of  $u_{,a}$ . Thus we easily obtain a theorem on the uniqueness of the solutions of the equation:  $K[u] = f(x^r)$ , with Cauchy-type conditions for  $u$  prescribed on  $R$ .

c. It should be noted that the third of the assumptions (16), which makes estimation (19) possible, is of essential importance; e. g. the equation

$$u_{tt} - \Delta u - \frac{u}{\sin t} + u = 0$$

has a non-trivial solution  $u = \cos t - 1$ , vanishing together with its partial derivatives on the hyperplane  $t = 0$ . This example shows also that the assumption  $|Q| \leq MI^0$  is essential for the truth of the theorem.

The author is greatly indebted to G. Plebański for his help while this paper was in course of preparation.

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# Note on Coulomb Effects in Stripping Reactions

by

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*Presented by L. INFELD on April 16, 1955*

Coulomb corrections to the Butler cross-section for the  $(d, p)$  and  $(d, n)$  reactions were recently [1] discussed with the help of the "zero-range" Horowitz-Messiah approximation for the  $n-p$  interaction. The integrations in the matrix elements were performed with the help of complicated numerical computations.

It appears that on applying the H.-M. approximation and the asymptotical exponential form of the wave function of the captured particle in the particular case of the  $S$ -state in the one-particle model, one can calculate analytically the Born approximation matrix element for the  $(d, p)$  or  $(d, n)$  reaction with the plane waves replaced by the Coulomb wave functions.

Let us consider first the  $(d, p)$  reaction. The usual Born approximation c. m. differential cross-section may be written in the form:

$$(1) \quad \sigma(\theta) = \frac{M_d^* M_p^* k_p}{(2\pi\hbar^2)^2 k_d} \frac{1}{3(2I_i + 1)} \sum_{\substack{\mu_p \mu_d \\ \mu_i \mu_f}} \left| \int d\sigma_n d\sigma_p d\xi d_{(3)} \bar{r}_n \chi_f^*(\xi, \bar{r}_n \sigma_n) \chi_i(\xi) e^{ik_d \bar{r}_n} \cdot e^{-ik_p' r_n} \int d_{(3)} \bar{q} e^{-ik_q} V_{np}(q) \psi(q) S_{\mu d}(\sigma_n, \sigma_p) \right|^2,$$

where  $M_d^*$ ,  $M_p^*$  are the deuteron and proton reduced masses;  $k_d$ ,  $k_p$  their respective momenta;  $\mu_p$ ,  $\mu_d$ ,  $\mu_i$ ,  $\mu_f$  — magnetic numbers;  $I_i$  — total angular momentum quantum number of the initial nucleus;  $\sigma_n$ ,  $\sigma_p$  — spin variables of the neutron and the proton;  $\bar{r}_n$  — vectors from the initial nucleus ( $i$ ) to the neutron and  $q$  — the vector from the neutron to the proton;  $\bar{k}_p' = \frac{M_i}{M_f} \bar{k}_p$  and  $\bar{K} = \frac{k_d}{2} - \bar{k}_p$ ;  $\chi_i$  and  $\chi_f$  are the internal wave functions of the initial and final nuclei;  $V_{np}(q)$  is the  $n-p$  interaction and  $\psi(q) \cdot S_{\mu d}(\sigma_n, \sigma_p)$  — the deuteron internal wave function.

On assuming the Mayer shell (one-particle) model we may write:  $\chi_f(\xi, \bar{r}_n, \sigma_n) = \chi_i(\xi) \Phi(\bar{r}_n, \sigma_n)$ ; if the neutron is captured to the  $S$ -state we have:  $\mathcal{Q}(\bar{r}_n, \sigma_n) = \mathcal{Q}(r_n) \chi_{\mu_n}(\sigma_n)$ . In this non-Coulomb case we obtain:

$$(2) \quad \sigma(\theta) = \frac{M_d^* M_p^* k_p}{(2\pi\hbar^2)^2 k_d} \cdot S^2 \left| \int d_{(3)} \bar{r}_n \mathcal{Q}(r_n) e^{i\bar{k}_d r_n} \cdot e^{-i\bar{k}'_p \bar{r}_n} \cdot \int d_{(3)} \bar{\varrho} e^{-i\bar{k}'_d \bar{\varrho}} V_{np}(\varrho) \psi(\varrho) \right|^2,$$

where the constant factor

$$S^2 = \frac{1}{3} \sum_{\mu_p, \mu_d, \mu_n} \left| \int d\sigma_n d\sigma_p \chi_{\mu_n}^*(\sigma_n) \chi_{\mu_p}^*(\sigma_p) S_{\mu_d}(\sigma_n \sigma_p) \right|^2$$

(in our case  $I_i = 0$ ).

On applying the H.-M. approximation we obtain a constant value for the integral over  $\bar{\varrho}$ . The only remaining integral is:

$$(3a) \quad I_x = \int d_{(3)} \bar{r} \Phi(\bar{r}) e^{i\bar{k}_d \bar{r}} \cdot e^{i\bar{k}'_p \bar{r}},$$

On replacing the plane waves by the respective Coulomb wave functions, we obtain:

$$(3b) \quad I_x^c = \int d_{(3)} \bar{r} \Phi(r) F_d(\bar{r}) F_p^*(\bar{r}),$$

where:

$$F_d(\bar{r}) = e^{-\frac{\pi n_d}{2}} \Gamma(1 + i n_d) e^{i\bar{k}_d \bar{r}} {}_1F(-i n_d, 1; i(k_d r - \bar{k}_d \bar{r}))$$

$$F_p^*(\bar{r}) = e^{-\frac{\pi n_p}{2}} \Gamma(1 + i n_p) e^{-i\bar{k}'_p \bar{r}} {}_1F(-i n_p, 1; i(k'_p r + \bar{k}'_p \bar{r}))$$

$$n_d = \frac{Ze^2 M_d^*}{\hbar^2 k_d}, \quad n_p = \frac{Ze^2 M_p^*}{\hbar^2 k_p}$$

${}_1F$  is the confluent hypergeometrical function.

On assuming

$$\Phi(r) = \sqrt{\frac{\gamma}{2\pi}} e^{-\gamma r}, \quad \gamma = \sqrt{\frac{2\mu_n \epsilon_n}{\hbar^2}}$$

( $\epsilon_n$  — binding energy of the captured neutron),

we can calculate  $I_x^c$  analytically by the Sommerfeld method [2]:

$$I_x^c = I_x e^{-\frac{\pi}{2}(n_p + n_d)} \Gamma(1 + i n_p) \Gamma(1 + i n_d) \left\{ \frac{k_d^2 - k_p'^2 + \gamma^2 - i 2\gamma k_d}{\kappa^2 + \gamma^2} \right\}^{i n_p}$$

$$\cdot \left\{ \frac{k_p'^2 - k_d^2 + \gamma^2 - i 2\gamma k_d}{\kappa^2 + \gamma^2} \right\}^{i n_d} {}_2F_1 \left( -i n_d, -i n_p, 1; \lambda \sin^2 \frac{\theta}{2} \right),$$

where  $\kappa = \bar{k}_d - \bar{k}'_p$ ,  ${}_2F_1$  is the hypergeometrical function,  $\lambda$  is a real number  $< 0$ , which it is convenient to represent in the form:

$$\lambda = \frac{4k_d k_p [(k_d + k_p)^2 - \gamma^2 + i2\gamma(k_p' + k_d)]}{(k_p'^2 - k_d^2 + \gamma^2 - i2\gamma k_d)(k_d^2 - k_p'^2 + \gamma^2 - i2\gamma k_p')} \quad \text{and} \quad \theta = \angle(\vec{k}_d, \vec{k}_p')$$

(the scattering angle).

The ratio of the cross-section resulting from (3b) to  $\sigma(\theta)$  is:

$$(4) \quad \frac{\sigma^c(\theta)}{\sigma(\theta)} = e^{-\pi(n_p + n_d)} \frac{\pi n_p}{sh\pi n_p} \frac{\pi n_d}{sh\pi n_d} e^{n_p \arctg \frac{2\gamma k_p'}{\gamma^2 + k_d^2 - k_p'^2}} \cdot e^{n_d \arctg \frac{2\gamma k_d}{\gamma^2 + k_p'^2 - k_d^2}} \left| {}_2F_1 \left( -in_d, -in_p, 1; \lambda \sin^2 \frac{\theta}{2} \right) \right|^2$$

Equation (4) gives a flattening of the angular distribution at larger angles and a very considerable decrease in the absolute values of the cross-section sensitive to  $Z$  and to the velocities of the deuteron and the proton.

As an illustration let us consider the reaction  $^{16}\text{O}(d, p)^{17}\text{O}^*$ , when the first excited state is formed ( $S$ -state,  $Q$ -value 1.04 MeV). The corresponding angular distributions  $\sigma(\theta)$  and  $\sigma^c(\theta)$  for smaller angles are indicated in Fig. 1 for the incident deuteron energy 4.5 MeV.  $\sigma^c(\theta=0)/\sigma(\theta=0) \cong 0.02$  for 4.5 MeV deuterons. The calculated  $\sigma^c(\theta=0) \cong 13.1 \frac{mb}{ster}$  is evidently too small in view of the

experimental value obtained by Burge et al. [3] for  $\theta=15^\circ$  and 7.73 MeV deuterons  $\sigma_{exp}(\theta=15^\circ) \sim 50 \frac{mb}{ster}$

and especially in view of the theoretically predicted reduction of the cross-section so as to include an interaction between the proton and the bombarded nucleus [4]. It seems that this discrepancy is mostly connected with neglect of the important (especially for smaller energies) probability of a compound nucleus formation and also with neglect of the Oppenheimer-Phillips process (i. e. the Coulomb deformation of the deuteron function  $\psi(\varrho)$ ). In any case, it appears to be certain that it is impossible to make a reasonable comparison between the absolute values of  $\sigma(\theta)$  and the values obtained experimentally, without taking into consideration the Coulomb effect.

On neglecting the Coulomb deformation of the internal wave function  $\phi(r)$  or the captured proton in the case of the  $(d, n)$  reaction, we would have for  $\sigma^c(\theta)/\sigma(\theta)$  eq. (4) with  $n_p=0$ ;  $\sigma^c(\theta)/\sigma(\theta)$  would be isotropic and the absolute values would be considerably greater (though of the same order) than for the  $(d, p)$  reaction with the neglect of the O.P. process.

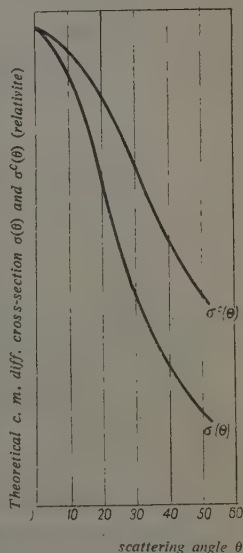


Fig. 1. Theoretical angular distribution of protons from  $^{16}\text{O}(d, p)^{17}\text{O}^*$  for incident deuteron energy 4.5 MeV:  $\sigma^c(\theta)$  — Coulomb effect included,  $\sigma(\theta)$  — no Coulomb effect

Further, the  $(d, n)$  processes arising from the compound nucleus formation are more probable than the corresponding  $(d, p)$  processes. The resultant probabilities of all the discussed processes would change the ratio  $\sigma_{dp}^c/\sigma_{dp}^c$ .

A somewhat similar situation is seen in the case of the  ${}^6\text{Li}(n, \alpha){}^3\text{H}$  reaction. This reaction was recently [5] investigated from the point of view of the " $\alpha$ -particle + deuteron" model with the assumption that the " $\alpha + d$ " system is in the  $S$  state.

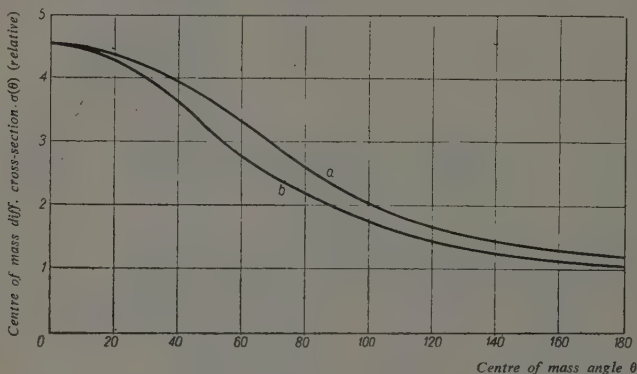


Fig. 2. Angular distribution of tritons from  ${}^6\text{Li}(n, \alpha){}^3\text{H}$  for incident neutron energy 1.5 MeV:  $a$  — experimental (Weddel and Roberts [12]),  $b$  — theoretical.

The Born approximation differential cross-section in the c. m. system for this reaction was obtained in [5] in the form:

$$(5) \quad \sigma(\theta) = \frac{M_t^* M_{n_0}^*}{(2\pi\hbar^2)^2} \frac{k_t}{k_{n_0}} \left[ \frac{1}{2 \cdot 3} \sum_{\mu_0, \mu_d, \mu_t} |\langle \chi_\alpha \chi_t e^{i\vec{k}_t(\vec{r}-\vec{s})} | V_{n_0d} | \psi_0 \rangle|^2 \right],$$

where:  $M_t^* = 12/7 M$ ,  $M_{n_0}^* = 6/7 M$  are respectively the triton and the neutron reduced masses;  $\vec{k}_t$  and  $\vec{k}_{n_0}$  are the corresponding momenta in the c. m. system;  $\mu_i$  are the resp. magnetic quantum numbers,  $\chi_\alpha = \chi_\alpha(\xi)$  is the internal wave function of the  $\alpha$ -particle,  $\chi_t = S_{\mu_t}(\sigma_0, \sigma_n, \sigma_p) \cdot R_t(s, u)$  — of the triton,  $\sigma_i$  being the corresponding spin variables;  $\vec{s} = \frac{\vec{r}_n + \vec{r}_p}{2} - \vec{r}_{n_0}$ ,  $\vec{u} = \frac{\sqrt{3}}{2} (\vec{r}_n - \vec{r}_p)$  are the internal co-ordinates of the triton;  $\vec{r}$  — is the vector from the  $\alpha$ -particle to the deuteron;  $V_{n_0d}$  is the incident neutron-deuteron interaction.  $\psi_0$  is defined by

$$\psi_0 = \chi_{\nu_0}(\sigma_0) e^{i\vec{k}_{n_0}(\frac{2}{3}\vec{r}-\vec{s})} \chi_\alpha(\xi) S_{\nu_d}(\sigma_n \sigma_p) \psi\left(\frac{2}{3}u\right) \Phi(r).$$

$\psi(\varrho)$  is the unperturbed deuteron internal function and  $\Phi(r)$  is the  $S$ -state " $\alpha + d$ " system internal function.

Now we shall not apply the transformation of the matrix element as was done in [5], but the "zero-range" interaction

$$V_{n_0d} = -\frac{3\pi a_{nd}\hbar^2}{M} \delta(\bar{s}), \quad \text{where} \quad a_{nd} = \frac{2}{3} \overline{a_4^2} + \frac{1}{3} \overline{a_2^2} \cong 5.08 \cdot 10^{-13} \text{ cm.}$$

the  $n$ - $d$  "scattering length" given by Christian and Gammel [7], as was done in [6] \*).

As a result we have:

$$\frac{1}{2 \cdot 3} \sum |< >|^2 = \frac{1}{4} \left( \frac{3\pi a_{nd}\hbar^2}{M} \right)^2 |b_k|^2 \cdot |I_t|^2,$$

where

$$b_k = \int R_t(u, 0) \psi\left(\frac{2}{3}u\right) d_{(3)}\bar{u} \quad \text{and} \quad I_t = \int \Phi(r) e^{i\bar{K}r} d_{(3)}\bar{r},$$

where

$$\bar{K} = \frac{2}{3} \bar{k}_{n_0} - \bar{k}_t.$$

Since the Coulomb interaction of the " $a+d$ " system is small (see e. g. [8]), the Coulomb deformation of  $\Phi(r)$  is neglected \*\*). Similarly, as in [9], we shall apply for  $\Phi(r)$  the asymptotical form  $\sqrt{\frac{\bar{\alpha}}{2\pi}} \frac{e^{-\bar{\alpha}r}}{r}$ , where  $\bar{\alpha} = \sqrt{\frac{2M}{\hbar^2} \epsilon}$  ( $\epsilon = 1.477 \text{ MeV}$  = the binding energy of the deuteron in the  ${}^6\text{Li}$  nucleus).

Let us now discuss the Coulomb effect of the outgoing triton wave in (5). The Coulomb polarization of the strongly bound structure of the triton is neglected.

On putting the Coulomb wave function in place of the triton plane wave in (5), we obtain, instead of  $I_t$ :

$$(6) \quad I_t^c = \int \Phi(r) e^{i\frac{2}{3}\bar{k}_n r} F_t^*(r) d_{(3)}\bar{r},$$

\*) The "zero-range" approximation is reasonable for neutron energies considerably less than 10 MeV; here it is equivalent mathematically to the H.-M. approximation.

\*\*)  $\Phi_c(r) = \frac{A}{r} W_{-n, \frac{1}{2}}(2\bar{\alpha}r)$ , where  $n = \frac{2e^2 M_d^*}{\hbar^2 \bar{\alpha}}$  and  $W_{-n, \frac{1}{2}}$  is the Whittaker function,

would be the corresponding function to  $\Phi(r) = \Phi_a(r) = \sqrt{\frac{\bar{\alpha}}{2\pi}} \frac{e^{-\bar{\alpha}r}}{r}$  if the internal Coulomb effect of the " $a+d$ " system were taken into consideration. Similarly as in [1] (Appendix 2),  $\Phi_c(r)$  may be approximated in the important region of  $r$  by some  $\Phi_a(r)$ . The value  $\alpha' = 3.34 \cdot 10^{12} \text{ cm}^{-1}$  may be calculated according to the method used in [1], if  $\bar{\alpha}' = 3.08 \cdot 10^{12} \text{ cm}^{-1}$ . The small difference between  $\alpha'$  and  $\bar{\alpha}$  has little effect on  $\sigma(\theta)$  and  $\sigma_c(\theta)$ .

where:

$$F_t^*(\vec{r}) = e^{-\frac{\pi n_t}{2}} \Gamma(1 + i n_t) e^{-i \vec{k}_t \vec{r}} {}_1F(-i n_t, 1; i(k_t r + \vec{k} \vec{r})), \quad n_t = \frac{2e^2 M_t^*}{\hbar^2 k};$$

The last integral is:

$$I_t = e^{-\frac{\pi n_t}{2}} \Gamma(1 + i n_t) \cdot I_t \cdot \left\{ \frac{\frac{4}{9} k_{n_0}^2 - k_t^2 + \bar{a}^2 - i 2 \bar{a} k_t}{K^2 + \bar{a}^2} \right\} i n_t$$

and the ratio of the cross-section resulting from (3) to  $\sigma(\theta)$ :

$$(7) \quad \frac{\sigma^c(\theta)}{\sigma(\theta)} = \frac{|I_t^c|^2}{|I_t|^2} = e^{-\pi n_t} \frac{\pi n_t}{s \hbar \pi n_t} e^{-2 n_t \arctg \frac{2 \bar{a} k_t}{k_t^2 - \frac{4}{9} k_{n_0}^2 - \bar{a}^2}}.$$

The angular distribution remains unchanged. However, as can be seen from Fig. 1, the agreement with experimental results of the angular distribution for 1.5 MeV neutrons is quite good (considerably better than that in [5]).

We can conclude then that the "zero-range" interaction, wiping out the factor  $I_h$  from [5], is even a better approximation for small energies.

Similarly as in [1] the comparison between the absolute values of  $\sigma(\theta=0)$  and  $\sigma^c(\theta=0)$  is more important. The values of these quantities for 1.5 MeV neutron energy are shown in Table I for 3 cases:

1)  $R_t$  — the Gaussian function used in [10] and  $\psi$  — the usual square well deuteron function,

2)  $R_t$  — the same as in 1) and  $\psi$  — the Hulthén function with the parameter values given by Chew and Goldberger [11],

3)  $R_t$  — the Irving function defined in [12] and  $\psi$  — the same as in 2).

TABLE I

	1	2	3
$\sigma(\theta=0)$	215.3	222.1	196.1
$\sigma^c(\theta=0)$	94.7	97.7	86.3

$\sigma(\theta=0)$  and  $\sigma^c(\theta=0)$  in  $\frac{mb}{ster}$  for 1.5 MeV neutrons.

The ratio  $\sigma^c/\sigma$  is equal, for neutron energies of 1.5, 2 and 14 MeV, to 0.44; 0.43 and 0.62 respectively. The use of  $\Phi(r) = \sqrt{\frac{a}{2\pi}} \frac{e^{-ar}}{r}$  gives too great  $\sigma(0)$ . In [5] the value  $\sigma(0) = 72 \frac{mb}{ster}$  for 1.5 MeV neutrons was obtained for the best for small energies " $a-d$ " interaction radius  $R_0 = 4 \cdot 10^{-13}$  cm.,  $R_t$ -Gaussian and  $\psi$  — Hulthén. Since the corresponding experimental

value [13] is  $\sigma_{\text{exp}}(0) = 46 \frac{mb}{\text{ster}}$ , on extrapolating our result  $\sigma^c/\sigma \cong 0.44$  to the approximation of [5], we would obtain a better agreement with experiment, for the absolute value.

Further, we see that  $\sigma^c/\sigma$  increases together with the neutron energy. In [5] too low values of  $\sigma(0)$  were obtained for 14 MeV neutrons. A much better (greater) value of

$$[\sigma(\theta=0)]_{14}/[\sigma(\theta=0)]_{1.5}$$

is hoped for as a result of the Coulomb effect.

I am much indebted to Professor L. Infeld for his kind interest in this work and to J. Dąbrowski for many helpful discussions.

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## The Energetic Part of the $\gamma$ -Ray Spectrum of ThD Determined with the Aid of a Diffusion Cloud Chamber

by

S. WIKTOR

*Communicated by H. NIEWODNICZAŃSKI at the meeting of March 28, 1955*

In the  $\gamma$ -ray spectrum accompanying the natural radioactivity of elements of the thorium series, the most energetic is commonly considered to be the line with an energy of 2.62 MeV, emitted by ThD ( $^{208}_{82}\text{Pb}$ ). However, there are a few results of experimental investigations which indicate that in the natural radioactivity of thorium there exists a line of still greater energy, viz., 3.20 MeV. The investigations of Alichanov and his co-workers [1], [2], carried out with the aid of a magnetic  $\beta$ -ray spectrograph with pair electrons produced by  $\gamma$ -rays from a ThC source, point to the existence of the 3.20 MeV line. Its relative intensity with respect

to the well-known strong line at 2.62 MeV was evaluated as being about 1:40. The nuclear emulsion method applied recently to this problem by Niewodniczański and Wielowiejska [3] confirmed the existence of the 3.20 MeV line. For its intensity relative to that with an energy of 2.62 MeV a value of about 1:10 was found. The purpose of the present work was to give further confirmation of the existence of the 3.20 MeV line in the  $\gamma$ -ray spectrum of ThD and to measure the relation of its intensity to that of the 2.62 MeV line with the use of a new method based on a diffusion cloud chamber.

A source of photo-neutrons (Fig. 1) was situated near a diffusion chamber which served for observing and photographing the tracks of recoil protons produced by collisions of neutrons with hydrogen nuclei inside the chamber. The chamber (Fig. 2) consisted of a glass cylinder,

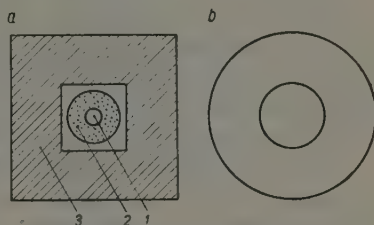


Fig. 1. *a* — neutron source, *b* — diffusion chamber; 1. MsTh. 2. Be. 3. Pb

25 cm. in diameter and 7 cm. in height. The walls of the cylinder were 8 mm. thick. The bottom of the chamber was made of a blackened aluminium plate, 6 mm. thick. The top cover, made of a brass plate 5 mm. thick, contained an externally heated methyl alcohol vapour source and was provided with a glass window for observation. The top cover together with the alcohol container were kept at a constant temperature, in the region of 20-25° C, by the flow of water from an ultra-thermostat through a spiral tube. The bottom of the chamber was cooled by solid carbon dioxide (so-called dry ice). The connections of the glass cylinder with metal plates were insulated with rubber.

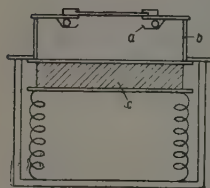


Fig. 2. *a* — vapour source, *b* — glass cylinder, *c* — dry ice.

In order to remove the excessive ions which were produced in the chamber in very great numbers by the strong  $\gamma$ -radiation from the source, a sweeping electrostatic field (voltage of about 500 V) was continuously maintained between the bottom and the cover. The sensitive region of the chamber occupied a volume extending from the bottom to a height of about 3 cm. The source of photo-neutrons consisted of about 20 m Curie of  $\text{MsTh}$ , surrounded by a layer (2.8 cm. thick) of powdered beryllium metal. This source was shielded from the chamber by a 10 cm. layer of lead. This thickness of the Pb shield was found experimentally to be the most suitable for reducing the background of  $\gamma$ -radiation in the chamber while, at the same time, it did not diminish too much the intensity of the neutron beam.

The chamber, working under atmospheric pressure, was filled with air and an admixture of hydrogen which was admitted continuously into the chamber in a weak stream. In the sensitive region of the chamber there appeared in the course of an hour an average of about 250 tracks of recoil protons and of background  $\alpha$ -rays produced from radioactive contaminations.

The energy of the recoil protons was determined by measuring the lengths of their tracks in the chamber. If the energy of the  $\gamma$ -ray photon amounts to 2.62 MeV, then taking into consideration the threshold energy for the reaction  ${}^9\text{Be}(\gamma, n){}^8\text{Be}$ , amounting to 1.67 MeV, and the recoil energy of the  ${}^8\text{Be}$  nucleus, amounting to 0.12 MeV, the liberated neutron should acquire a kinetic energy of 0.83 MeV. Similarly, the 3.20 MeV photon should transfer 1.36 MeV of kinetic energy to the liberated neutron. In the case of a head-on collision we can assume that the neutron transfers its total energy to the recoil hydrogen nucleus. In air, under normal conditions, the range of 0.83 MeV protons is, according to Livingston and Bethe [4], 17 mm., while that of 1.36 MeV protons is 37 mm. The 37 mm. tracks were distinctly visible among the many 17 mm. tracks directly observed and photographed.

Owing to the small efficiency of the neutron source and the limited time of exposure, the number of photographed tracks was too small to ensure a more exact estimation of the intensity of both  $\gamma$ -ray lines. The recoil proton tracks were then counted visually. During counting, the tracks were divided into two groups: those of the 1st group having approximate length ranging from 5 to 20 mm., and those of the 2nd group from 20 to 40 mm. Tracks deviating from the direction of the neutron beam at an angle greater than  $45^\circ$ , were not counted. The second group contained also tracks produced by the  $\alpha$ -rays from gaseous radioactive contaminations. Most of these tracks were produced by the  $\alpha$ -rays of radon and possessed a maximum length slightly exceeding 40 mm. In order to distinguish these tracks from those due to proton recoils, the track counting was performed repeatedly under the same experimental conditions, only with the beryllium powder removed.

The total time taken to count the tracks in the chamber was 2145 minutes. During this time 6926 tracks were recorded. The results of the counting are given in the following table:

TABLE

	Total number of tracks observed		$\alpha$ -ray background		Difference (protons)	
		Mean number per hour		Mean number per hour		Mean number per hour
Duration of recording (min).	1305	—	1140	—	—	—
Number of tracks of the 1st group	4704	216	95	5	4595	211
Number of tracks of the 2nd group	1348	62	779	41	458	21

The ratio between the number of proton tracks in the 2nd group and the number in the 1st group is 1:10. In order to find the ratio between the number of photons with an energy of 3.20 MeV and those with an energy of 2.62 MeV emitted in the same time interval by the MsTh source, it is necessary to take into account the dependence of the cross-section of  ${}^9\text{Be}$  nuclei for the reaction  ${}^9\text{Be}(\gamma, n){}^8\text{Be}$  on the  $\gamma$ -ray energy as well as the dependence of the cross-section for elastic scattering of neutrons by protons upon the energy of the former. At the same time the small difference in absorption and scattering of photo-neutrons of the energies 0.83 MeV and 1.36 MeV by lead was not taken into consideration. The resulting intensities ratio of the lines at 3.20 MeV and at 2.62 MeV was evaluated as being about 1:12.

The histogram in Fig. 3 shows the results of photographing the recoil tracks. 1179 photographs were taken and these gave 530 tracks suitable for measuring. The lengths of the tracks were measured by projecting the negatives onto a screen and comparing the lengths of the proton tracks with that of a scale which was simultaneously photographed. Only tracks which were inclined to the direction of the neutron beam by not more than  $45^\circ$  and which were placed approximately in a hori-

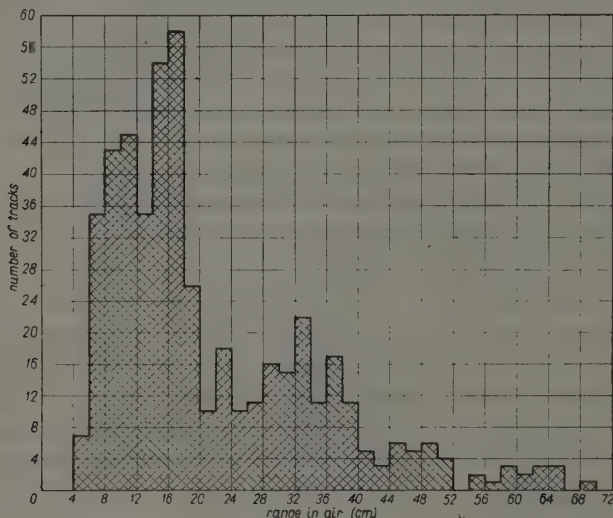


Fig. 3

zontal plane were measured. In Fig. 3 two groups of proton recoil tracks with lengths around 17 mm. and 37 mm. corresponding to the  $\gamma$ -ray energies 2.62 MeV and 3.20 MeV, may be distinguished. This histogram contains also  $\alpha$ -ray tracks of radon, thoron and probably even actinon, all of them exceeding 37 mm. The purpose of producing Fig. 3 is solely to show the existence of the  $\gamma$ -radiation with an energy of about 3.20 MeV emitted by ThD.

The author wishes to express his gratitude to Professor H. Niewodniczański for suggesting this problem and for giving much helpful advice in the course of the work.

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## Titanic Acid Gel as an Adsorption Layer in Potentiometric Chromatography

by

B. KAMIEŃSKI and I. MAZUR

*Communicated by B. KAMIEŃSKI on April 5, 1955*

The smaller the volume of the electrolyte dividing the indicator electrode from the reference electrode, the greater is the influence of traces of external substances upon the electrode potential. The minimal mass of the electrolyte is obtained when the volume is reduced to a thin layer of silicic acid gel. The layer adsorbs traces of gases contaminating the atmosphere, and the electrode potential changes rapidly. The smaller the volume of the electrolyte, the greater is its resistance, and since layers of silicic acid are weak conductors of electricity, an electrometer of small capacity must be applied when checking the potential of the electric micro-element.

This sensitive electrode is composed of a thin metallic wire fused into a glass rod. The ground cross-section of the rod discloses the end of the wire which serves as an electrode. A thin silica gel layer is put on the cross-section of the wire and forms the electrolyte as described in previous papers by B. Kamiński [1]–[6]. The element which may be composed of a platinum, or antimony, wire and a reference electrode (e. g. a calomel electrode), provides an efficient apparatus for measuring the hydrogen ion concentration of the solution flowing out of the adsorption tube or for indicating slight traces of gases contaminating the atmosphere [2], [3], [7].

On the basis of the theory of adsorption [8], [9], it may be supposed that the gel of titanic acid, on account of its greater dielectric constant, will adsorb gases from the air more readily than the gel of silicic acid. The principles of electrostatics make it possible to calculate the change of energy accompanying the adsorption from air (or vacuum) of an electric charge  $e$  contained in a sphere of diameter  $a$  into a phase of a dielectric constant  $K_s$  (silicic acid gel) or into another phase of a dielectric constant  $K$ ,

(titanic acid gel). The change is

$$\frac{2e^2}{a} - \frac{2e^2}{aK_s} = \frac{2e^2}{a} \left(1 - \frac{1}{K_s}\right),$$

or

$$\frac{2e^2}{a} - \frac{2e^2}{aK_t} = \frac{2e^2}{a} \left(1 - \frac{1}{K_t}\right).$$

Subtracting the equations we get

$$\frac{2e^2}{aK_t} - \frac{2e^2}{aK_s} = \frac{2e^2}{a} \left(\frac{1}{K_t} - \frac{1}{K_s}\right),$$

which corresponds to the energy of transferring the electric charge (ion) from the silicic acid gel to the titanic acid gel. Taking into account the dielectric constant of titanic acid which is much greater than that of silicic acid (rock crystal has two constants, viz., 4.69 and 5.06, rutile 89 and 173), we may suppose that the gel of titanic acid will be a more efficient adsorbent. The antimony electrode (antimony wire fused into a glass rod) was covered with a very thin layer of dried titanic acid gel and the action of the electrode compared with another antimony electrode covered with a thin layer of silicic acid gel as described in former papers.

The titanic acid gel was prepared in the following way: 1 g. of titanic acid was mixed with 10 c. cm. of hydrochloric acid (sp. gr. 1.19). After 10 days the clear part of the solution was analysed. One c. cm. of the titanium chloride solution contained 9.43 mg. of titanic dioxide. A small quantity of the solution was necessary to carry out hydrolysis and to dialyze titanium chloride, and one fourth of a cubic centimetre was diluted with distilled water to the volume of 50 c. cm.; 16 c. cm. of the dilute solution were dialyzed for 15 days by changing the water twice daily. The meniscus of the solution was kept higher than that of the distilled water.

After 15 days no chloride ions were present and the volume increased to about 21 c. cm. Some of the titanic acid conglomerated in a sediment and milling of the colloidal solution was necessary before applying a drop to the end of the antimony electrode; the drop dried at room temperature, and a thin layer of titanic acid gel was formed at the bottom end of the glass rod antimony electrode. The reference electrode was an antimony electrode wetted with a solution of 0.1 N potassium chloride. This element was very sensitive to different gases. In this case the vapours of acetic acid were used. A square sheet of filter paper, 2 cm.  $\times$  2 cm., was saturated with acetic acid and placed at the bottom of a glass tube 7 cm. high and 4 cm. in diameter. The end of the electrode was placed at a distance of 6 cm. from the filter paper lap. The potential of the electrode changed rapidly and equilibrium was established after some time. When the potential was stable, ammonium carbonate (1 gram) was put into

the glass tube in place of the saturated filter paper. The potential changed again, but in a reverse direction.

The purpose of the experiment was to ascertain whether a layer of titanic acid gel is a more efficient adsorbent than a layer of silicic acid gel. The mass of the layer was very small, as may be realized when we consider that only one drop of the solution was applied to the end of the glass rod electrode and dried to form the gel. One drop of silica gel contained  $5.7 \cdot 10^{-5}$  g. of silica whereas one drop of titanium gel contained  $2.8 \cdot 10^{-7}$  g. of titanium dioxide. Figs. 1 and 2 show

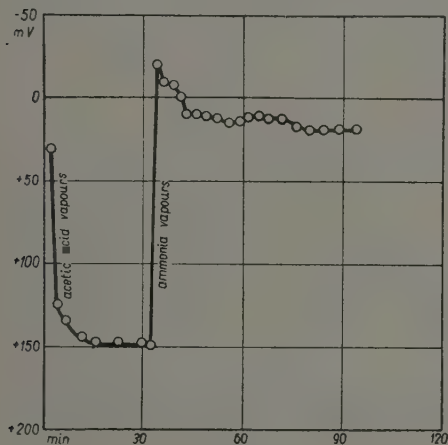


Fig. 1.

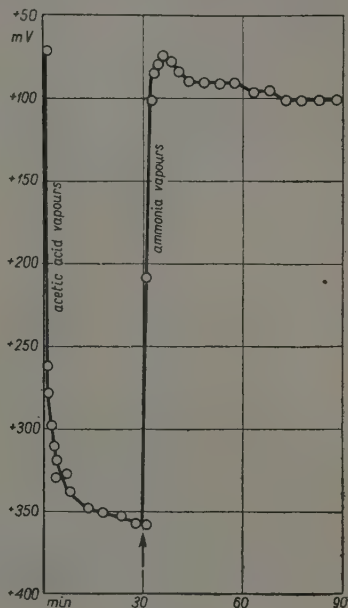


Fig. 2.

the changes in the potential millivolts on the ordinate, time on the abscissa) when silica gel (Fig. 1) and titanic acid (Fig. 2) were applied. The changes observed in the potential were greater when a layer of titanic acid gel was applied, as may be seen in Fig. 2; when the silica gel was applied to the electrode, the device became less sensitive, as may be seen in Fig. 1. The respective changes in the potential were 170 mV (Fig. 1), and 280 mV (Fig. 2). The above measurements confirm the supposition in regard to the influence of the dielectric constant. In the respective gels the mass of titanium dioxide was about 200 times smaller than the mass of silica but, in spite of this fact, the titanic gel was a more efficient adsorbent.

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## The Rôle of Vanadyl Sulphate in the Process of Catalytic Oxidation of Sulphur Dioxide

by

S. WEYCHERT and J. LEYKO

*Presented by S. BRETSZNAJDER on April 13, 1955*

Investigation of the synthesis and decomposition of vanadyl sulphate was carried out by the flow method in a temperature ranging from 360–630°, using a thermobalance. The reagents were chemically pure  $V_2O_5$  and air containing 10–45%  $SO_2$ .

In some experiments the gases were first passed through another furnace containing a vanadium catalyst, so that some of the  $SO_2$  underwent conversion to  $SO_3$  before the gases reached the reactor proper. In some of the last experiments  $V_2O_5$  was reduced by pure  $SO_2$ .

The progress of the synthesis or decomposition of  $VOSO_4$  was followed by reading the deflections of the thermobalance; the degree of conversion of  $SO_2$  was determined by analysis of the gases leaving the reactor.

It was found that not all of the  $V_2O_5$  present could be converted to  $VOSO_4$ , even if equilibrium conditions were exceeded. The degree of conversion of  $V_2O_5$  continually rose with the temperature.

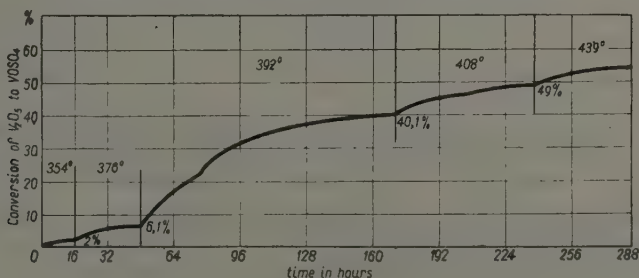


Fig. 1.

Only when the temperature exceeded a certain value did the decomposition of  $VOSO_4$  begin. This critical point depended but slightly on

the velocity and composition of the gases and on the conditions under which synthesis of  $\text{VOSO}_4$  had been previously carried out. Decomposition proceeds gradually with increasing temperature. At 10–20° above the initial temperature the decomposition is complete. The diagrams on

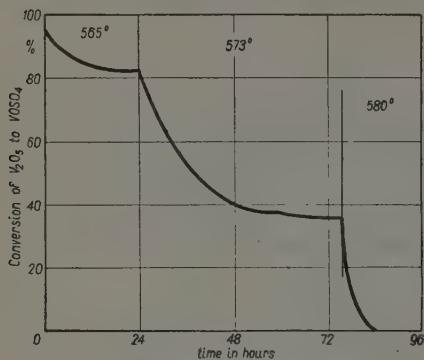


Fig. 2.

Figs. 1 and 2 illustrate the course of one of the experiments of this type.

We observed that at lower temperatures reaction took place in the whole mass of  $\text{V}_2\text{O}_5$ , as shown by the uniformly distributed greenish tint. In spite of this, however, not all of the  $\text{V}_2\text{O}_5$  present underwent conversion. On the contrary, when synthesis was carried out at higher temperatures, or when a partial decomposition of previously formed  $\text{VOSO}_4$  was achieved,

we obtained differently coloured pellets, their colour depending on their position in the bed (those placed nearer the gas-inlet were amber-coloured ( $\text{V}_2\text{O}_5$ ), the others — green ( $\text{VOSO}_4$ )).

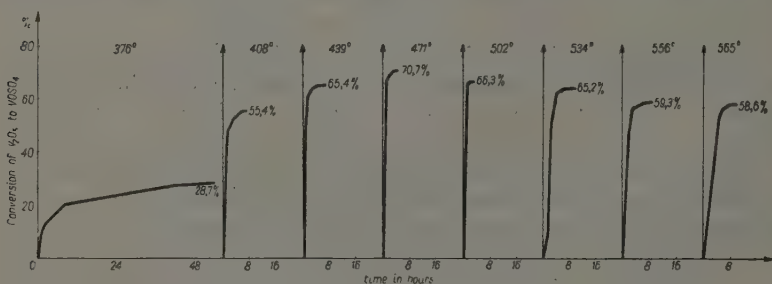


Fig. 3.

The course of some experiments on the synthesis of  $\text{VOSO}_4$  from  $\text{V}_2\text{O}_5$ ,  $\text{SO}_2$  and  $\text{O}_2$  at constant temperatures is illustrated by the diagrams in Fig. 3.

Curves are drawn from left to right according to the increasing temperatures of successive experiments.

It is evident from the diagram that the degree of conversion of  $\text{V}_2\text{O}_5$  to  $\text{VOSO}_4$  was at first higher in each successive experiment, but after passing a maximum became lower and lower as the temperature was raised further.

In each of these experiments the rate of  $\text{VOSO}_4$  formation was at first very high, being in fact of the same order as the rate of oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ . However, when a certain degree of conversion was achieved, the reaction slowed down and very soon practically came to a standstill.

The initial rate was highest in experiments 2, 3, 4 and 6. In experiments performed at the lowest (1) and the highest (7 and 8) temperatures, it was visibly lower.

The numerical values of initial velocities are given in Table I.

TABLE I  
The rate of  $\text{VOSO}_4$  synthesis in experiments 1–8

No. of exp.	1	2	3	4	5	6	7	8
Temperature °C	376	408	439	471	502	534	556	565
Rate of synthesis ml. $\text{SO}_2$ /hr./1 g. $\text{V}_2\text{O}_5$	24.2	130	142.7	148.2	148.9	123.3	79.2	30.2

When gases were used, which had been already partly oxidised, it was possible to convert the whole mass of  $\text{V}_2\text{O}_5$ . However, this was achieved only when the equilibrium conditions for  $\text{VOSO}_4$  stability were markedly exceeded.

We also found that the rate of synthesis of  $\text{VOSO}_4$  was considerable, being not lower than that of the catalytic oxidation of sulphur dioxide. Under the conditions of our experiments the synthesis rate was nearly constant within a large range of temperatures. In Table II are given the numerical values of reaction rates corresponding to experiments conducted at different temperatures.

TABLE II  
The rate of  $\text{VOSO}_4$  synthesis with previous oxidation of  $\text{SO}_2$

Degree of conversion of inlet-gases	20%	20%	20%	20%
Temperature °C.	376	439	534	565
Rate of synthesis ml. $\text{SO}_2$ /hr./1 g. $\text{V}_2\text{O}_5$	156.6	148.1	151.6	75.5

In the experiments on reduction of  $\text{V}_2\text{O}_5$  when pure  $\text{SO}_2$  was used, it was observed that at lower temperatures  $\text{VOSO}_4$  was at first formed. Later, in the course of the experiment it underwent decomposition to  $\text{V}_2\text{O}_4$ . At higher temperatures  $\text{V}_2\text{O}_4$  was formed directly.

In both cases the reaction rate was low.

### Conclusions

1. For the formation of vanadyl sulphate from  $V_2O_5$  and gases containing  $SO_2$  and  $SO_3$  or  $SO_2$  and  $O_2$  the equilibrium conditions must be considerably exceeded, especially at lower temperatures.

Contrary to other authors, we have shown the equilibrium conditions to be quite inadequate for  $VOSO_4$  synthesis. It is not certain if this is caused by the extremely high decomposition pressures of the vanadyl sulphate nuclei, which are formed on the surface of the dispersed and highly active phase of  $V_2O_5$ .

2. The rate of formation of  $VOSO_4$  from  $V_2O_5$  and from gases containing  $SO_2$  and  $SO_3$  is very high. In gases containing  $SO_2$  and  $O_2$  the rate is also high, being of the order of the rate of catalytic oxidation of  $SO_2$ . This is in direct contradiction to Boreskov's statement, that the rate of  $VOSO_4$  formation is low.

3. It was confirmed that the reaction of  $V_2O_5$  with  $SO_2$ , and  $O_2$ , giving  $VOSO_4$  as a product, did not go on to completion, in spite of the fact that the conditions corresponded to equilibrium.

This may be explained by the fact that the conditions necessary for  $VOSO_4$  synthesis can be realised only when a high degree of  $SO_2$  to  $SO_3$  conversion is achieved.

At low temperatures this is realised only inside the capillaries and at high temperatures in those layers of reacting material which are far from the gas-inlet.

The establishment of these facts should have a bearing on the methods and results of calculation of the ignition temperature of the contact process.

4. Further investigation is needed to explain the causes of the very high rate of  $VOSO_4$  formation during the contact process. This rate probably exceeds the rate of the whole process of  $SO_2$  oxidation (ending in desorption of  $SO_3$ ).

5. The reduction of  $V_2O_5$  to  $V_2O_4$  proceeds very slowly even at high temperatures.

At low temperatures it is accompanied by the formation of  $VOSO_4$ . As this reaction is controlled by the former one, its rate is also very low.

The assumption that the formation of  $VOSO_4$  which accompanies the reduction of  $V_2O_5$ , proceeds with no previous  $SO_3$  desorption leads to the conclusion that the rate of synthesis of  $VOSO_4$  as a whole should be controlled by the first stages of reduction.

It follows that the rate of the first stages of reduction is very low. This, in turn, excludes the possibility that reduction of  $V_2O_5$  (not even in its first stages when  $SO_3$  has not yet been desorbed and the proper crystalline phase of  $V_2O_5$  formed) could be one of the stages of the usual contact process.

## On the Distillation Anomalies Observed in Mixtures of Components Forming Ternary Positive-Negative Azeotropes and Zeotropes. I

by

W. ŚWIĘTOSŁAWSKI and W. TRĄBCZYŃSKI

*Communicated by W. ŚWIĘTOSŁAWSKI at the meeting of May 16, 1955*

**1. Observations of Ewell and Welch.** In 1945 some interesting phenomena were described by Ewell and Welch [1] with regard to ternary systems in which two of the components formed with each other a binary negative azeotrope and with the third, a ternary zeotropic or azeotropic mixture. Owing to the shape of the tridimensional boiling temperature isobar ( $p=1$  atm.), a top-ridge curve divided the Gibbs triangle of concentrations into two parts. Only one system, that composed of chloroform, acetone and methanol, formed a positive-negative azeotrope. The latter still represents a unique example of a ternary saddle azeotrope which does not contain water. According to the classification suggested by one of us [2], it belongs to the first group, and its formation is due to the differences in the van der Waals forces acting between the molecules of the three components.

The anomaly taking place in the course of a fractional distillation of mixtures, forming systems characterised by the presence of a top-ridge condensation temperature isobar consists in the forming of several distillation levels, one of which, found in the middle or not far from the last level, is characterised, by a lower condensation temperature than that of the two neighbouring ones.

Several years later Lang [3] confirmed the existence of these anomalies. In both the above-mentioned papers, however, no observations were made with regard to the changes in composition of the fractions collected and of the bottom products remaining after each successive removal of the distillate. Another paper of Haase and Lang did not contain either sufficient data [3]. Because of that, no graphical presentation could be made of the gradual changes in the composition of the fractions collected and of mixtures found in the flask and in the column.

**2. Behaviour of Ternary Positive-Negative Azeotropes Belonging to the Second Group.** The purpose of the present investigation was to examine the behaviour of a new group of ternary positive-negative azeotropes formed by a weak organic (acetic) acid,  $A$ , a weak organic (pyridine) base,  $P$ , and a hydrocarbon,  $H$ . In our case this last was the normal octane. Starting with 1952, a relatively large number of ternary saddle azeotropes of this kind were examined in our laboratory and some of them were described [4], [5], [6], [7]. They did not contain water and the negative azeotrope  $[(-)A, P]$  was formed as a result of the chemical acting forces of an acid and a base.

For the first example there was chosen a saddle azeotrope in which the top-ridge condensation temperature isobar lay not far from the line  $HC$ , as shown in Fig. 1. In addition, the point  $(\pm)Az$ , corresponding to the composition of the ternary saddle azeotrope, is located closer to point  $H$  and somewhat higher than point  $M_P$ , which lies also on the top-ridge curve but corresponds to the maximum convexity of the top-ridge line. Its location is higher compared with other mixtures represented graphically by the same top-ridge curve  $HM_P C$ .

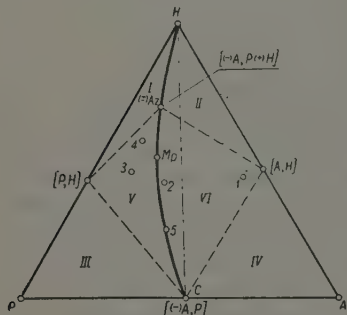


Fig. 1. Distillation fields of a ternary positive-negative azeotrope  $[(-)A, P(+ )H]$ ; all of them, except V and VI, form triangles. Fields V and VI are separated by the top-ridge curve  $H(\pm)Az M_P C$ . It is assumed that section  $H(\pm)Az$  is practically a straight line.

There is another factor which exerts an influence on the distillation anomalies in the case of the saddle azeotropes examined in our laboratory. It consists in the large variety in shapes of the top-ridge condensation temperature isobars and in the locations of point  $(\pm)Az$ , corresponding to the composition of the ternary positive-negative azeotropes. In this investigation we chose the case graphically presented in Fig.1.

**3. Distillation Curves and Material Balance of Distillate Fractions and Mixtures Remaining in the Flask and in the Column.** In Fig. 1, points 1, 2, 3, 4 and 5 represent the respective compositions of the initial mixtures submitted to fractional distillation. All details concerning these five distillations, including the analytical methods used for determining the compositions of the numerous fractions collected, will be published elsewhere. In this paper are described the most interesting experiments observed in the course of fractional distillation of the mixtures represented by points 4 and 5.

The distillation curves are shown in Figs. 2a and 2b. The concentration triangles are presented in Figs. 3a and 3b; in each of them curves I

and *II* correspond to the compositions of the fractions collected (*I*) and of the remaining material (*II*) found in the flask and in the distilling column.

It should be noted that point 4 lies between points  $(\pm)Az$  and  $M_P$ . Point 5 is located on the top-ridge curve below  $M_P$ .

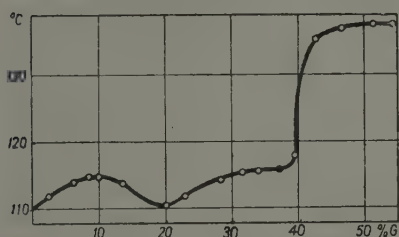


Fig. 2a

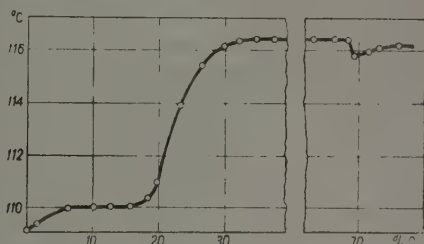


Fig. 2b

Figs. 2a and 2b. Distillation curves of mixtures 4 and 5. No horizontal level corresponding to the boiling temperature of the positive azeotrope  $[P, H]$  is found on curve 2b. A pronounced temperature decrease corresponds to the moment when the total reflux has been established in the column.

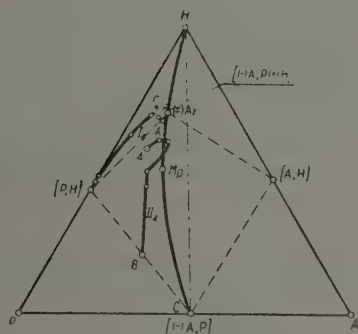


Fig. 3a

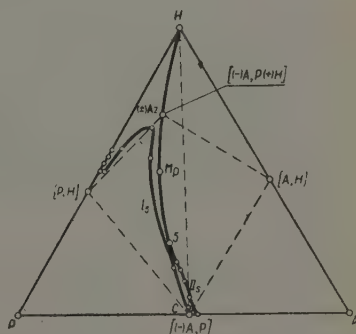


Fig. 3b

Figs. 3a and 3b. The compositions of the fractions collected when distilling mixtures 4 and 5, are shown on curves  $I_1$  and  $I_2$ , and those of the bottom mixtures found in the flask and in the column (hold-up) are represented by curves  $II_1$  and  $II_2$ .

At the beginning of the fractional distillation of mixture 4 the positive binary azeotrope  $[P, H]$  was collected in the receiver. Section *A* on the "bottom product curve"  $II_4$  is practically a straight line. In the next stage the fractions collected (section *C* on curve  $I_4$ ) have the composition equal or nearly equal to that of the ternary saddle azeotrope  $(\pm)Az$ . The flat surface of this part of the tridimensional isobar, as well as the analytical errors in determining small amounts of the fractions collected must be considered as responsible for the dissipation of the points lying in the flat regions. At this stage of the distillation, the com-

position of the mixture found in the flask and in the hold-up of the column underwent changes, so that at the end of the distillation point  $B$  was reached. This point lies practically on the straight line connecting point  $[P, H]$  with  $[(-)A, P]$ . At that moment there was not enough liquid to continue the distillation. One may assume, however, that a "straight line" distillation would have been followed, associated with a new drop in the condensation temperature. This would be associated with the distillation of azeotrope  $[P, H]$  and afterwards with that of the negative one.

The fractional distillation of mixture 5 has been associated with the particularities shown in the graph of the two curves  $I_5$  and  $II_5$  (Fig. 3b). No horizontal levels were found in the course of the fractional distillation represented by the curve in Fig. 2b. Instead, a series of middle fractions appeared, which corresponded to mixture of  $[P, H]$  and  $(\pm)Az$  with an excess of the positive azeotrope in the first stage, and a decrease in the concentrations of  $[P, H]$  in the second stage. Afterwards, the saddle azeotrope  $(\pm)Az$  was collected and at the end of the distillation a mixture very similar to the composition of the negative azeotrope was found in the distillate.

The shape and the location of curve  $II_5$  show the compositions shifting towards the left side of the main line  $HC$ . This corresponds to the higher concentrations of acetic acid compared with the last sections of curve  $I_5$ . It is probable that some thermal decomposition of the liquid in the flask was responsible for this shifting. It may be, however, that during that part of the distillation a new anomaly had appeared so that more pyridine passed into the receiver during the last stages of the distillation. Owing to this, both curves  $I_5$  and  $II_5$  have been shifted to the left side of the triangle.

It should be noted that a relatively large section of the distillation curve  $I_5$  practically merged with the top-ridge condensation temperature isobar  $HM_P C$ .

We wish to express our thanks to W. Michałek for helping us with the distillation experiments and with the analytical work.

#### Summary

1. The recently investigated new group of ternary, positive-negative azeotropes, containing a weak organic acid, a weak organic base and a hydrocarbon, shows distillation anomalies similar to those found for a known saddle azeotrope composed of chloroform, acetone and methanol ( $I$ ).

2. The saddle azeotropes  $(\pm)Az$ , containing acetic acid,  $A$ , pyridine,  $P$ , and normal octane,  $H$ , contains less pyridine than the mixture represented by point  $M_P$ , which lies on the top-ridge isobar and corresponds to the mixture characterised by its maximum convexity. The top-ridge curve is located closer to the main line  $HC$  as compared with azeotrope  $[P, H]$ .

3. The material balance of the fractions collected (curves  $I_4$ ,  $I_5$ ) and of the mixtures remaining in the flask and in the column (curves  $II_4$ ,  $II_5$ ) was presented graphically in Figs. 3a and 3b for the two most interesting cases (points 4 and 5 in Fig. 1)

4. In the case of the fractional distillation of the mixture represented by point 4, it was found that at the end of the distillation the bottom product in the flask corresponded to a mixture of the negative azeotrope  $[(-)A, P]$  and the positive one,  $[P, H]$ . The last section of curve  $II_4$  is a straight line inclining under an acute angle to the main line  $HC$ .

5. The fractional distillation of mixture 5 (Fig. 1), represented by point 5 lying lower than  $M_P$  showed abnormal distillation phenomena in the first stage of the distillation. At the end, both the last fractions collected ( $I_5$ ) and the mixtures found in the flask after each partial distillation ( $II_5$ ) were shifted towards higher concentrations of acetic acid ( $A$ ) as compared with the content of  $A$  in the negative azeotrope formed by  $A$  and  $P$ . It may be that this phenomenon was associated with some thermal decomposition of the residue in the flask.

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DEPARTMENT OF PHYSICAL CHEMISTRY OF ORGANIC RAW MATERIALS

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## A New Quantitative Classification of Clastic Rocks

by

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*Presented on February 24, 1955*

Statistical studies have shown that the earth's sedimentary crust is composed primarily of such elements as clay — 82%, sands — 12%, and carbonates — 6% [1]. Particular quantitative combinations of these minerals are characteristic for certain definite kinds of clastic rock. In the course of geological surveys many such groups have been so far recognised, and their significance and importance as historical evidence are constantly increasing.

Today the classification of the clastic elements in the crust of the earth is a problem of ever growing importance, as was once the case with igneous rocks. It is a question of arranging in an orderly way the abundant material already identified, and although the significance of this problem has been recognized, no satisfactory arrangement of the material has yet been advanced, in spite of the numerous attempts undertaken in various research centres [2] [3] [4]. The reason for such a state of affairs is twofold: on the one hand, it lies in the nature of the material to be classified, while on the other, it is connected with the modern requirements of the natural sciences which stress, and rightly so, that any classification in this field should be based on quantitative analysis, since only such analysis can supply historic and genetic evidence.

It is also, of course, evident that the classification of clastic rocks should be based primarily on a quantitative analysis of the minerals of which the rocks are composed. In the case of igneous rocks this method has not only proved most successful, but is now the generally accepted one. It seems, therefore, most appropriate and natural that this course should be followed also when attempts are made to classify clastic rocks. Such attempts should take into account the fact that the most common kinds of rocks are composed of clay, sand (broadly speaking), and carbonates (calcite, dolomite).

Theoretically, all quantitative combinations of these three elements are possible in the composition of the sedimentary rocks here discussed.

Not all combinations, however, characterise some particular environment. The principal factors in the formation of groups are the morphological features of the sedimentary basin and the corresponding gravitation conditions. Thus, reciprocally, the quantitative combination of the elements in the elastic rocks should characterize the morphological features as a function of these features. From what has been said, therefore, it follows that an adequate classification system would include the characteristic features of the sedimentary environment.

In Poland, the first attempt at working out a classification system conforming to the required standards was made by K. Smulikowski [5], who divided elastic rocks into groups represented by corresponding and quantitatively defined sectors of a concentration triangle — clay, carbonates, and sand being placed at the vertices of this triangle. The triangle, devised by Smulikowski, greatly resembles Johannsen's model [6] worked out for the classification of igneous rocks.

In the present paper the author presents a new model of the concentration triangle, in which none of the three rock components (clay, sand, or carbonates) is privileged as the basis for classification. Such a procedure is consistent with the natural conditions. The three mineral elements from sedimentary rocks are placed at the vertices of the triangle. In "pure" clays, sands (sandstones and quartzites), and carbonates (limestones and dolomites) — the monomineralic rocks actually existing in the earth's crust — there are undoubtedly factors which make a definition of the characteristic features of their environment possible. For classification purposes the "purity" of the components is reduced to a conventionally accepted value equal to a 10% content of the other components (Fig. 1, sectors 1, 2, and 3). Consequently, the sides of the triangle correspond to the two-mineral rocks: sand-clay, clay-carbonates, and carbonate-sand (Fig. 1, sectors 4 to 12). According to the conventional agreement just made, the presence in these sectors of up to 10% of the third component is accepted in the course of identification. The most significant parts of the sides of the triangle seem to be those which lie half way between two vertices; there, rocks are grouped with equal or nearly equal quantities of two of the components (Fig. 1, sectors 5, 8 and 11). For this reason they are consistently marked out in the projection in all three outer bands of the triangle.

Outlined in the central area of the triangle is sector No. 22, which comprises rocks with equal, or approximately equal, quantities of all three components. This is the sector of marly rocks.

The definition of marly rocks is, unfortunately, one of the least precise in geology and petrography, hence, by the introduction of a strict quantitative definition for the mineral ratios of the marls some precision will at once be achieved. Moreover, the sedimentary environment,

where such rocks are formed, becomes defined more accurately than was possible previously.

Adjacent to the area representing marls are three other triangles (Fig. 1, sectors 19, 20, and 21) with their vertices pointing to the vertices of the outer triangle. In these are grouped marly rocks in which clayey, sandy, or limy components are predominant. This is stressed by the names applied to these sectors, viz., sandy marls (19), clayey marls (20), and limy marls (21).

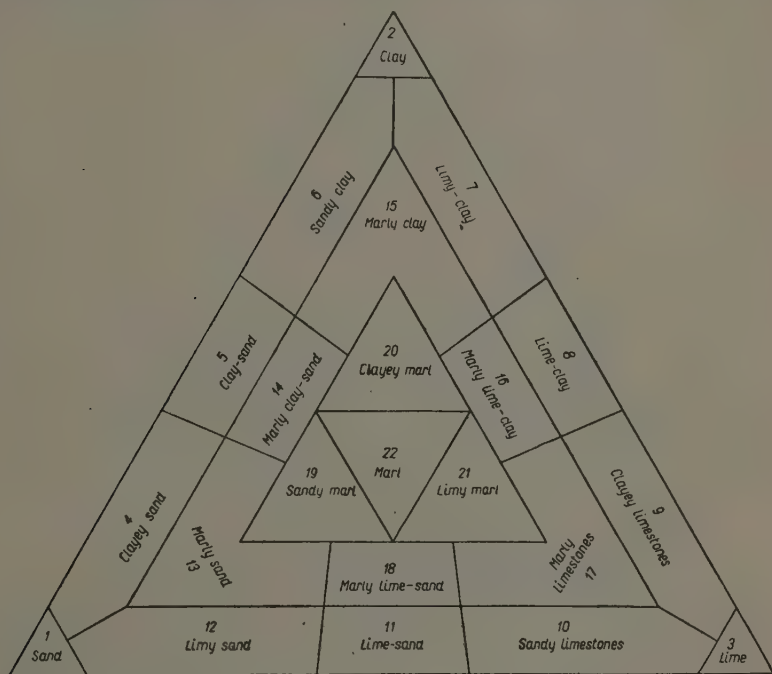


Fig. 1

Finally, between the outer bands already referred to and the inner triangles representing marly rocks three intermediate bands are marked out; these differ from the outer bands by a conventionally accepted 10 – 20% content of the third component (Fig. 1, sectors 13 to 18). The whole of the triangle is thus divided into three concentration triangles, one inside the other. The consistent principle of classification is, therefore, differentiation of the three quantitative variants: the monomineral, two-mineral, and three-mineral materials. Obviously, the decimal system agreed upon here is only conventional, and quite certainly the rocks found in nature have no need to conform to it. Hence, the classification here described is devised for practical purposes and is intended to faci-

litate the distinction of groups in the clastic rocks and, what is even more important, to help those whose job it is to study such rocks.

By applying the method here described, all clastic rocks are divided into four classes, while every class is subdivided into orders, the total number of which is 22.

The general pattern of the classification is illustrated in the appended table, and the two concentration triangles in Figs. 1 and 2.

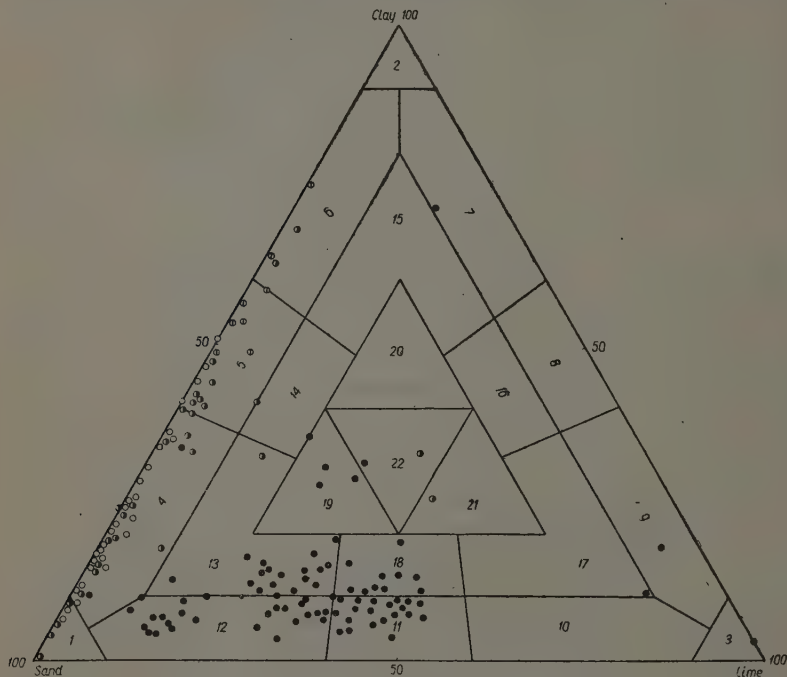


Fig. 2

The classification is based — as has already been stated — on a quantitative mineral analysis of the clastic formations.

In research work on clastic rocks no accurate methods have so far been devised for carrying out the necessary analyses.

The microscopic (planimetric) techniques, very useful for research on the composition of igneous rocks, cannot always be applied in the case of clastic rocks, because of the often undefined nature of the component elements. However, the analytic technique developed recently by the author and defined as "thermal analysis" [7] is very suitable for this purpose. This technique enables us to determine with a considerable degree of accuracy the mineral composition of the rocks under

## CLASSIFICATORY TABLE

(S — Sand, Cl — Clay, Cb — Carbonates)

## Class I. Monomineral Rocks

(Chief component 100—90%, others 0—10%)

Order 1.	Sands (sandstones, quartzites etc)	S <sub>100-90</sub>
Order 2.	Clay (clay, shale etc)	Cl <sub>100-90</sub>
Order 3.	Carbonates (limestones, dolomites)	Cb <sub>100-90</sub>

## Class II. Two-mineral Rocks

(Two chief components 100—90%, the third 0—10%)

Order 4.	Clayey sand (sandstones etc)	S <sub>90-60</sub>	Cl <sub>5-40</sub>
Order 5.	Clay-sand (loam)	S <sub>60-40</sub>	Cl <sub>10-60</sub>
Order 6.	Sandy clay	S <sub>40-5</sub>	Cl <sub>60-90</sub>
Order 7.	Limy-clay	Cl <sub>90-60</sub>	Cb <sub>5-40</sub>
Order 8.	Lime-clay (dolomite, clay)	Cl <sub>60-40</sub>	Cb <sub>40-60</sub>
Order 9.	Clayey limestones (dolomites)	Cl <sub>40-5</sub>	Cb <sub>60-90</sub>
Order 10.	Sandy limestones (dolomites)	S <sub>40-5</sub>	Cb <sub>5-90</sub>
Order 11.	Lime-sand	S <sub>60-10</sub>	Cb <sub>40-60</sub>
Order 12.	Limy sand (sandstones etc)	S <sub>60-90</sub>	Cb <sub>40-5</sub>

## Class III. Three-mineral Rocks

(Two components 80—20%, the third 10—20%)

Order 13.	Marly sand (sandstones etc)	S <sub>80-50</sub>	Cl <sub>10-35</sub>	Cb <sub>10-35</sub>
Order 14.	Marly clay-sand	S <sub>55-35</sub>	Cl <sub>35-30</sub>	Cb <sub>10-20</sub>
Order 15.	Marly clay	S <sub>10-35</sub>	Cl <sub>50-80</sub>	Cb <sub>10-30</sub>
Order 16.	Marly lime-clay	S <sub>10-20</sub>	Cl <sub>30-55</sub>	Cb <sub>35-55</sub>
Order 17.	Marly limestones	S <sub>10-35</sub>	Cl <sub>10-35</sub>	Cb <sub>50-80</sub>
Order 18.	Marly lime-sand	S <sub>35-55</sub>	Cl <sub>10-20</sub>	Cb <sub>30-55</sub>

## Class IV. Marly Rocks

(Three components 20—60%)

Order 19.	Sandy marl	S <sub>40-60</sub>	Cl <sub>20-40</sub>	Cb <sub>20-40</sub>
Order 20.	Clayey marl	S <sub>20-40</sub>	Cl <sub>40-60</sub>	Cb <sub>20-40</sub>
Order 21.	Limy marl	S <sub>20-40</sub>	Cl <sub>20-40</sub>	Cb <sub>40-60</sub>
Order 22.	Marl	S <sub>20-40</sub>	Cl <sub>20-40</sub>	Cb <sub>10-40</sub>

investigation, and is based on a quantitative estimation of the dehydration, oxidation, and dissociation processes which take place at various temperatures.

This method has been applied in hundreds of cases and has always proved most useful [8], [9], especially for purposes of comparison.

The value of the techniques introduced in this paper for obtaining a rational classification of elastic rocks is demonstrated here by plotting analytical results in the concentration triangle (Fig. 2). The material used for this purpose was obtained in the course of thermal analyses carried out on two series of elastic samples. In one of the series the samples came from known oligocene sandstones forming the geological profile of the Krosno district in the Carpathians. In the other series the same analytic techniques were applied to various kinds of sandy soils collected in the Cracow area; this series also included fractions of less than two microns (defined in soil science as "colloids") which have been analysed and reported separately.

The tabulated numerical results obtained analytically for the experimental material are not given, because the three-component parameters for every analysis can easily be deduced from the projection.

About 500 analyses were carried out on samples obtained from strata in the Krosno district, but not all the results were plotted in the triangle, as many of them coincided completely or very nearly so (black spots).

The soils from around Cracow (diluvial and alluvial) are indicated by the half-shaded circles. The empty circles correspond to the analytical results of alluvial soils from the Vistula valley in Goczałkowice, while the "soil colloids" are represented by the bisected circles.

### Conclusions

When the distribution in the concentration triangle of the points representing the various kinds of detrital materials is considered carefully, the following conclusions may be drawn:

1. The analyses of the sandstones from the Krosno district give results grouped very closely together, chiefly in sectors 11, 12, 13 and 18. This indicates that, in principle, those materials correspond lithologically to the four systematically distinct orders known as lime-sands, limy sands, marly sands, and marly lime-sands. Some of the samples from the Carpathians correspond to sector 19, defined as sandy marls. One analytical result corresponds to order 22 (marl), two others to order 4 (clayey sand), one to order 7 (limy-clay), one to order 9 (clayey limestones), and, finally, one result corresponds even to order 3 ("pure carbonates").

In this manner the sedimentary environment in which these Flysch formations originated is defined by the quantitative mineral composition of the rock elements as shown by the concentration triangle. One out-

come of this investigation which seems especially significant is the singling out of elements from the whole series, which, by reason of their parameters, diverge markedly from the most common samples grouped in sectors 11, 12, 13, and 18. Such divergent elements may be considered as "indices" and may in future, have a practical application in the important problem of correlating the stratigraphic levels in the Carpathian oil-bearing series.

2. The points representing most of the analysed soils, alluvial soils, and "colloids" are closely grouped along the two-mineral sandelay sector. The drop in their fertility, as shown by the low level of calcium carbonate, is clearly visible. There is, however, one exception, viz., the diluvial soils from the Dolina Strążyska in the Tatra Mountains. The points representing these soils are grouped in the sectors corresponding to a high level of calcium carbonate (13, 14, 21, and 22). There is no doubt that because of this the soils are fertile (rendzines).

The analytical data presented here, obtained by thermal analysis based on the quantitative evaluation of the principal mineral components of the clastic rocks, fully confirm the value for research work on sedimentary rocks and their derivatives of the classification proposed in this paper.

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